PRODUCT OPTIMIZATION OF THE DIRECT CONVERSION PROCESS OF NATURAL GAS TO METHANOL BY CONTROLLED OXIDATION

FINAL REPORT

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EXECUTIVE SUMMARY

The direct conversion of methane to methanol is simpler and requires less energy than the presently used "synthesis gas method" which involves two catalysed reaction steps. The first step involves the catalytic steam reforming of methane, a highly endothermic reaction (+206.2 kJ mol^{-1}) requiring significant amounts of fuel (1). Coupled with the formation of methanol from synthesis gas the process is still energy intensive (ΔH overall = +115.4 kJ mol^{-1}).

In the direct conversion of methane to methanol, via controlled partial oxidation, there is a net gain of energy as the reaction is exothermic overall (-128.3 kJ mol^{-1}).

Previously we have been successful in experimentally producing methanol at a carbon selectivity of 80% or better, a minimum yield of 4% at methane conversions of 10% at the 5% oxygen level on a bench scale. Reaction conditions varied according to the reactant feeds (Methane/Natural gas and oxygen/air).

In the present contract the effects of sensitization, reactant flow mode, product feed recirculation (after removal of condensible liquid oxygenates) and kinetics of the oxidation reaction were studied in a series of tasks. The first task was concerned with the construction of a microreactor designed to operate in a) an equilibrium flow through mode and b) a pulsed plug flow mode. A methanol selectivity of 77% (based on carbon), in 3.4% yield at 4.4% conversion of methane, was the optimum value obtained with the reactor operating in the equilibrium flow through mode, at 430°C, 35 atm pressure and oxygen concentration of 3%. Higher yields and conversion but lower selectivity of methanol were

achieved at higher oxygen concentrations. The results obtained while operating in the pulsed plug flow mode were inconclusive due to excessive diffusion of the reactant pulse in the helium carrier gas. The resulting conversions were consequently very low (< 1%).

The introduction of sensitizers into the reaction system (generally incorporated into the pure methane feed) considerably affected the reaction conditions (Task 2) while maintaining high methanol selectivities in some cases. The best example of this was 2,3-dimethylbutane which at a concentration of 3%, with respect to methane, effected complete reaction at 10 atm pressure and 322°C producing methanol in selectivity of 77%. This compares with a minimum temperature for complete reaction (MTCR) of 410°C in the absence of the sensitizer at 10 atm reaction pressure. The use of hexane reduced the reaction temperature still further to 285°C but with methanol selectivity falling to 65%. Sensitization of the reaction, providing small enough quantities are used, could be an important factor in minimizing reactor heating costs because of the higher reaction temperature necessary in their absence. Higher hydrocarbon compounds may be found in such quantities in certain natural gases in addition to ethane and propane.

Sensitization can also occur by using external means such as ultra-violet radiation. In Task 3 it was demonstrated that such radiation generated by a mercury resonance lamp photosensitized the reaction to the extent that there was a 40% increase in oxygen utilization and methane conversion increased by 32%, compared to the situation in its absence at 390°C. The energy output of the lamp was

modest, however (7.5×10^{17} mL^{-1} s^{-1}) and a more powerful source of radiation such as a laser could have more pronounced effects (2).

At oxygen concentrations of 5.5 and 10% at 27 atm reaction pressure the rate constant for the oxidation of methane was determined from the Arrhenius parameters $k_r = 5 \times 10^{12} \exp(-2100/T)$ s^{-1}. Kinetic curves were determined assuming pseudo first order kinetics with the methane concentration remaining essentially constant.

Recirculation of the unconsumed methane feed was desirable to improve the conversion and methanol yield. Removal of condensible liquid products is obvious though removal of the other gaseous oxidation products of carbon monoxide and carbon dioxide was not necessary. However, the influence of carbon monoxide and dioxide build up on the oxidation reaction particularly with respect to methanol selectivity was not known. Results obtained using a bench scale Recirculation system showed that the selectivity of methanol was not adversely affected by high carbon monoxide and dioxide concentrations (30% of recycled input feed) particularly at higher conversions of methane. Operating at an initial methanol selectivity of 43% on a single pass basis and 9% conversion resulted in a methanol selectivity of 47% upon recirculation. At 70% methanol selectivity (single pass) and a conversion of 5% returned a selectivity of 63% during recirculation in the presence of carbon monoxide and carbon dioxide. These results demonstrate the insensitivity of the oxidation reaction to high levels of carbon monoxide and dioxide towards methanol selectivity which could considerably reduce the frequency of purging an industrial system and hence minimize costs due to lost feed.

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RÉSUMÉ POUR L'EXÉCUTIF

La mèthode de conversion directe du méthane en méthanol est plus simple et demande moins d'énergie que la méthode de synthèse gazeuse utilisée actuellement et qui implique deux étapes de réactions catalytiques. Le première étape consiste en "catalytic steam reformining" du méthane, réaction hautement endothermique (+206.2 kJ mol^{-1}) et demandant de grandes quantités de carburant (1). Couplé avec la formation du méthanol par synthèse gazeuse, le processus est encore énergétiquement intense (ΔH total = +115.4 kJ mol^{-1}).

Au cours de la conversion directe du méthane en méthanol, par oxydation partielle controlée, puisque la réaction est globalement exothermique (-128.3 kJ mol^{-1}), il y a un gain net d'énergie.

Précédemment, nous avons produit du méthanol expérimentalement avec succès avec une sélectivité en carbone de 80% et mieux, un rendement minimum de 4% avec des conversions en méthane de 10% et avec un niveau de 5% en oxygène à petite èchelle. Les conditions de réaction ont varié relativement aux apports de réactif (méthane/gaz naturel et oxygène/air).

Dans ce contrat, nous avons étudié les effects de sensibilisation à travers une série de tâches successives: système de flux du réactif, recirculation des produits carburants (après avoir oté les oxygénates liquides condensables) et la cinétique de la réaction d'oxydation. La première tâche fût la construction d'un microréacteur pouvant opérer:

a) avec un système en equilibre avec le flux et

b) avec un système à impulsion de flux.

Une sélectivité en méthanol de 77% (basée sur le carbone), avec rendement de 3.4% à 4.4% de conversion du méthane fut la valeur optimale obtenue avec la réacteur opérant avec le système en équilibre avec le flux à 430°C, 35 atm de pression et une concentration en oxygène de 3%. Une conversion et des rendements supérieurs ont été obtenus avec des concentrations supérieures en oxygène mais avec une selectivite inférieure en methanol. Les résultats obtenus en operant avec le système de flux "impulsé" ne sont pas concluants, ceci étant du à la diffusion excecive de l'"impulsion" de réactif dans l'helium gazeux

porteur. Les conversions résultantes furent par conséquent très bonnes (<1%).

L'introduction de "sensibilisateurs" dans le système réactif (généralement incorporés dans l'apport de méthane pur) ont considérablement modifié les conditions de réaction (tâche #2) tout en maintenant de hautes sélectivités en méthanol dans certains cas. Le meilleur exemple est le 2,3-diméthylbutane qui, à une concentration de 3% par rapport au méthane, effectue une réaction complète à 10 atm de pression et à 322°C produisant du méthanol avec une sélectivité de 77%. Ceci est comparable avec une température minimum pour une réaction complète (MTCR) de 410°C en l'absence de sensiblisateur à une pression de 10 atm. L'utilisation d'hexane réduit de plus la température de réaction à 285°C mais avec une sélectivité en méthanol tombant à 65%. La sensibilisation de la réaction, pourvu que de suffisanment petites quantités soient utilisées, pouvait être un facteur important dans la minimisation des coûts de chauffage du réacteur à cause de la température de réaction plus élevée qui est necéssaire en leur absence. Des composés hydrocarbonés supérieurs peuvent être trouvés en telles quantités dans certains gaz naturels en plus de l'éthane et du propane.

La sensibilisation peut également apparaitre en utilisant des moyens externes tel que la radiation ultra-violette. Dans la 3° tâche, il a été prouvé qu'une telle radiation produite par une lampe résonante au mercure a photosensibilisé la réaction jusqu'à un point tel qu'il y a eu un accroissement de 40% dans l'utilisation de l'oxygène et une conversion du méthane accrue de 32% comparativement à la situation en son absence à 390°C. Neanmoins l'apport énergétique de la lampe est modeste (7.5×10^{17} m L^{-1} s^{-1}) et une source plus puissante de radiation, tel que un laser, pourrait avoir des effets plus prononcés (2).

Avec des concentrations en oxygene de 5.5 et 10% à 27 atm de pression pour la réaction, la constante (rate) pour l'oxydation du methane a été déterminée a partir des parametres d'Arrhenius $k_r = 5 \times 10^{12} \exp(-2100/T)\ s^{-1}$. Les courbes cinétiques ont été déterminées par une vitesse de réaction du pseudo premier ordre et avec une concentration un méthane restant essentiellement constante.

La recirculation dans l'apport du méthane non consommé est recommandée en vue d'améliorer le rendement et la conversion en méthanol. Le retrait des produits liquides condensables est évident alors que le retrait des autres produits gazeux d'oxydation du monoxyde et du dioxyde de carbone n'est pas nécessaire.

Cependant, l'influence du monoxyde et du dioxyde de carbone lors de la réaction d'oxydation, particulièrement par rapport à la sélectivité du méthanol, n'est pas connue. Des résultats obtenus en utilisant un système à recirculation à petite échelle ont demontré que la sélectivité du methanol n'etait pas affectée considérablement par des concentrations élevées en monoxyde et dioxyde de carbone (30% de l'apport recyclé introduit) particulièrement pour des conversions élevées du méthane. En opérant avec une sélectivité initiale du méthanol de 43% sur la base d'un passage unique et 9% de conversion, il en a résulté une sélectivité en méthanol de 47% avec recirculation. Avec une sélectivité en méthanol de 70% (passage unique) et une conversion de 5%,il en a résulté une sélectivité de 63% pendant la reciruclation en présence de monoxyde et de dioxyde de carbone. Ces résultats démontrent l'absence de sensibilité de la réaction aux hauts niveaux de monoxyde et de dioxyde de carbone envers la sélectivité en méthanol qui peut réduire considérablement là fréquence de purge d'un systeme industriel et par là, minimiser les coûts dus a la perte des apports.

INTRODUCTION

This report is a summary of work continuing from the previous contract "Study of the Direct Oxidation of Natural Gas to Methanol", DSS File No. 22ST 23440-4-9011, Serial No. OST83-00404, submitted in April 1985.

The present contract sought to perform the following Tasks (modified form).

1. Construction of the Microreactor and Preliminary Experiments. To construct a Mircoreactor to operate in equilibrium flow through and plug flow modes and tested according to the procedure outlined in the literature.*
2. Sensitization Initiation. To study the sensitization of the methane oxidation reaction using homogeneous catalysts (sensitizers) and determine their effect on reaction parameters such as methanol selectivity and reaction temperature.
3. Sesitization Optimization. To select the more promising sensitizers and determine their effectiveness in greater detail in a large diameter (13 mm i.d.) glass lined reactor.
4. Hg Sensitization (modified Task). To design and construct a quartz reactor which would permit the transmission of ultra-violet radiation from a Hg resonance lamp and to study

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*Igarashi, A, and Ogino, Y, Techniques for High Pressure Catalysis Research. I. A Pulse Reactor with an in situ Gas Chromatograph, Applied Catalysis, 2, 339 (1982).

the sensitizing effect of this radiation on the methane oxidation reaction.

5(a). Determination of Kinetic and Arrhenius Parameters. To determine rates of formation of the products produced from the oxidation of methane with oxygen under a variety of reaction conditions and hence estimate the rate constant and activation energy for the reaction.

5(b). To conduct experimentation in which the oxidation of methane would be carried out operating in the recycle mode in the presence of carbon monoxide and carbon dioxide which would not be removed from the product stream prior to recirculation. To determine effect of the presence of these components on the formation of methanol.

These Tasks have been Completed

Canada has large reserves of Natural Gas which, if converted into a liquid form, would be of tremendous value as a fuel in Canadian industry.

Utilisation of these reserves in this way would reduce Canada's dependancy on crude oil which will ultimately be depleted in about 80-100 years despite new finds and as such have a positive effect on the Canadian economy.

The most straightforward liquid fuel derived from Natural gas is methanol and this would seem to be the answer to future energy and chemical needs worldwide. The literature supports this view (1) and indeed methanol is already a major commodity in world chemical production.

Presently the bulk of the methanol produced in Canada and around the world is derived from synthesis gas. This report is concerned with the continuing study of a direct conversion of natural gas to methanol and its optimization where plant cost and size would be reduced considerably using a homogeneous process. Much of Canada's natural gas reserves are in remote locations and the direct conversion of the gas would be possible by this method as smaller plants could be mobile and because of the versatility of the reaction towards reaction conditions. The operating pressure has been shown to be very flexible (10-125 atm) using the direct method and operating temperature can be modified using sensitizers (this Report).

This report is divided into five parts with each part covering each of the five tasks.

PART ONE

Construction of the Microreactor and Preliminary Experiments.

A) EQUILIBRIUM FLOW-THROUGH SYSTEM

INTRODUCTION

This section describes the construction of the microreactor assembly and the work carried out to establish the conditions of optimum yields during the partial oxidation of methane to methanol.

In all, 25 runs were carried out to evaluate the effect of process parameters such as temperature, pressure, feed gas composition and flow rate on the methane conversion and methanol selectivity. Prior to these runs a few experiments were conducted so as to set the pace for the rest of the study.

EXPERIMENTAL PROCEDURE

The microreactor together with the high pressure G.C. has been constructed. A flow diagram of the set-up is shown in Figure 1.1.

The reactor has an inside diameter of 0.65 cm into which a glass tube (0.63 cm o.d. x 0.36 cm i.d.) is inserted to form a close fit. The internal diameter of the glass tube, of 0.36 cm and a heated reaction zone of 30 cm, is equivalent to a reaction volume of 3.3 mL. The reactor was mounted vertically in an electric furnace and the temperature was controlled by a solid state digital temperature indicator/controller (Omega series CN300). The temperature in the

reaction zone was measured by a thermocouple probe (1/32" diameter) inserted into the reactor and connected to a temperature indicator.

Gases (2% N_2 in CH_4 and O_2) from the respective cylinders were pre-mixed before entering into the reactor by passing them through a mixing cross filled with Teflon turnings. The pressures at various points were monitored by calibrated pressure transducers (Validyne Model DP-1564) connected to a Validyne digital transducer indicator (CD 280-4 RM). The flow rates were indicated and controlled by mass flow controllers (Brooks 5800 series) connected to a dual channel control unit (Brooks Model 5876). The upstream reactor pressure was controlled using a vernier needle valve (Aerosmith V54-1-11) which was located following the 8-port gas sampling valve (Valco Instruments). A safety relief valve (Nupro adjustable) was installed at the entrance of the reactor and was set to open at a pre-set maximum pressure of 60 atm. In order to ensure that the flow of the gases is undirectional, check valves were installed in the gas lines before the mixing cross. The exit gases from the reactor outlet and the relief valve were vented outside to the atmosphere through 13 mm. copper pipes. The entire reactor assembly was pressure tested for 50 atm. Furthermore, the connecting lines between the reactor and GC were heated and well insulated to prevent condensation of products.

Helium at a pressure of 40 atm was used as the carrier gas for the GC analysis of the reaction products. The carrier gas was passed successively through the reference side of the thermal conductivity detector, 8-port gas sampling valve, column and into the sample side of the detector. The pressure of the carrier gas was reduced to atmospheric by means of a vernier needle valve which also served for

adjusting the flow rate. Finally, the carrier gas passed into a flame ionization detector, which permitted a high sensitivity analysis of organic compounds. The flow rate of the helium carrier gas was adjusted to 60 mL/min (at STP), so that the flame could be sustained. The reaction products were analysed using a molecular sieve 5A (0.9 m x 3 mm o.d.) and Porapak-S (3 m x 3 mm o.d.) columns. O_2, N_2 and CH_4 were separated on the molecular sieve column. On the other hand, oxides of carbon (CO, CO_2), water and methanol were separated on the Porapak-S column.

Further, the analog output from the temperature indicator (TI in Figure 1.1) was connected to a voltage recorder (Varicord Model 43) after passing through a voltage suppressor and range scale expander unit (Photovolt Model 7632). This enabled us to record the temperature oscillations observed during some of the experiments. The chart speed of the recorder was kept constant during the entire study at 2.5 cm/min and the full scale deflection on the chart (25 cm) corresponded to 1.226 mv or a rise in temperature of 29°C.

Conversion (based on CH_4 fed) was calculated from the molar ratios (CH_4/N_2) obtained upon analysing the reactor inlet and outlet streams on a molecular sieve 5A column. The selectivity of each of the carbon containing compound was calculated from the peak areas after correcting for sensitivities. The peak areas were obtained upon analyzing the reactor exit stream on a Porapak-S column. The expressions are as follows:

$$\text{Conversion (mol\%)} = \left[\frac{(CH_4/N_2)_{inlet} - (CH_4/N_2)_{outlet}}{(CH_4/N_2)_{inlet}}\right] \times 100$$

$$CH_3OH \text{ selectivity (mol\%)} = \left[\frac{\text{corrected peak area of } CH_3OH}{\Sigma \text{ peak areas of } CH_3OH, \text{ CO and } CO_2}\right] \times 100$$

$$CH_3OH \text{ yield (mol\%)} = CH_4 \text{ conversion} \times CH_3OH \text{ selectivity}$$

RESULTS

A summary of the process conditions employed during this study are presented in Table 1.1. The range of the variables were chosen on the basis of past experience (Gesser et al., 1985). The conversion, selectivities and methanol yield obtained during each of the experimental runs are tabulated in Table 1.2. Using the data in Table 1.2, a series of graphs (Figures 1.2-1.7) showing the effect of reaction temperature on methane conversion, methanol and CO selectivity, methanol yield and the effect of oxygen concentration in the feed gas on methanol selectivity are obtained.

Interestingly, during some of the runs, temperature oscillations were observed. It may be possible to correlate the frequency and amplitude of these temperature oscillations (not to be confused with thermal runaway) with the conversion and selectivity obtained during the partial oxidation process. As a result of this approach, the temperature oscillations have been recorded. Some of the salient features observed are briefly discussed below.

DISCUSSION

1. Effect of reaction temperature on methane conversion

As seen from Figure 1.2, methane conversion depends significantly on temperature, pressure and oxygen concentration. At a given set of conditions, conversion is found to increase with increase in temperature, reach a maximum and later decrease. On the other hand, low oxygen concentrations and feed gas flow rates seem to have a favorable

influence on the methane conversion. As seen from Figure 1.5, at higher temperatures, CO_2 selectivity is found to increase indicating that at these conditions concurrent oxidation of CO to CO_2 must be taken into account. Hence, as a result, the available O_2 is partly consumed by CO thus lowering methane conversion.

2. Methanol selectivity

Methanol selectivity seems to depend mostly on the oxygen concentration and reaction temperature as seen from Figures 1.3 and 1.4. At any given combination of process conditions, there appears to be a maximum value with respect to reaction temperature. However, this maximum is observed to depend on the other process conditions. As a rough guideline, it can be said that the temperature required to obtain maximum methanol selectivity shifts to lower temperature values at low oxygen concentrations. Our observations are in agreement with the thermodynamic and stoichiometric considerations which show that low temperatures, low O_2/CH_4 ratios and high pressures favour methanol selectivity.

3. CO selectivity

As seen from Figure 1.5, CO selectivity initially decreases with increase in reaction temperature up to a certain value and later increases with further rise in temperature. However, an exception to this trend was observed during run #15 (35 atm, 2.8% O_2, 25 mL/min) wherein CO selectivity remained nearly the same til around 430°C and later increased with increase in reaction temperature. At higher temperatures, the rates of methane oxidation to CO will be higher than

the rate of the reaction leading to the formation of methanol. Hence, higher temperatures favour CO selectivity as compared to methanol selectivity.

4. Temperature oscillations

It is well known that the gas-phase oxidation of organic compounds under certain conditions give rise to cool flames (Minkoff and Tipper, 1962). Cool flame is a brief chemilumiescence accompanying a rapid but short-lived increase in the rate of oxidation. Cool flame behavior depends on the pressure, temperature, feed gas composition, residence time and reactor geometry.

The characteristics of the temperature oscillations observed during some of the experiments are described in Table 1.3. The salient features are summarized as follows:

i) The frequency and amplitude of the temperature oscillations depend mostly on the O_2 concentration and initiation temperature.

ii) At the lower O_2 concentrations, no oscillations are observed.

iii) At a given set of conditions, oscillations are observed only at some intermediate initiation temperatures and at higher temperatures they are subdued.

iv) The frequency and amplitude of the oscillations are higher at the top of the reactor as compared to other locations in the reactor. It appears that along the length of the reactor, the cool flames decay.

v) An examination of the dependency of methanol selectivity and temperature oscillations show that higher selectivities are obtained at temperatures just below the onset of cool flames.

B) PULSE FLOW SYSTEM

In order to conduct the pulse studies, the experimental set-up shown in Figure 1.1 was slightly modified. The modified set-up is shown in Figure 1.8.

Helium at a pressure of 20 atm and a flow rate of 60 mL/min (NTP) was passed successively through the reference side of the thermal conductivity cell, the loop of 8-port gas sampling valve, micro-reactor, GC column (Porapak-S, 3 m x 3 mm o.d.) and into the sample side of the detector.

Pre-mixed gas containing 10 mol % O_2, 2 mol % N_2 and 88 mol % CH_4, at a total pressure of 16.5 atm and a flow rate of 30 mL/min (NTP) was passed continuously through the other loop of the 8-port gas sampling valve.

Once the steady-state reaction conditions were reached, the loops of the sample valve were interchanged such that 0.5 mL of the feed gas sample was flushed into the microreactor assembly.

Interestingly, upon analyzing the feed gas pulse it was found that the order of elution of the components (CH_4,O_2) was reversed to the order normally obtained (O_2,CH_4) on the Porapak-S column. Furthermore, the peaks were broad in contrast to the sharp peaks obtained in a routine analysis at atmospheric pressure.

The analysis of product stream at two different reaction temperatures of 315° and 404°C, showed only traces of CO, CO_2 and CH_3OH. This indicated that the conversion was too low.

It is possible that excessive dead volume could have resulted in an inefficient mixing of CH_4 and O_2 in the reactor zone, thus leading to a

very low conversion of methane to products. Hence, at this stage, further experiments were not conducted. However, it may be worthwhile to continue this type of study which can reveal the intrinsic kinetics (free from heat and mass transfer) of the partial oxidation of methane reaction, by minimizing the length of the connecting tubing and rearranging the experimental assembly in a very compact manner.

CONCLUSIONS

From the present study, the following conclusions are drawn:

1. In order to maximize selectivity (68-77 mol%), it is better to conduct the reaction at lower reaction temperatures (410-440°C) and oxygen concentrations (3-5 mol%) as possible.
2. Temperature oscillations offer a guideline to locate the region of maximum methanol selectivity.
3. Incorporation of the online high pressure GC technique seems to be advantageous in that problems such as product losses due to volatility could be minimized.
4. As seen from the study, the pulse flow reactor was found to have no particular advantage over the equilibrium-flow reactor. However, further work on the pulse reactor may help in elucidating detailed reaction kinetics of the partial oxdiation reaction.

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2. G. J. Minkoff and C. F. H. Tipper, Combustion Reactions, Butterworths, London (1962).

TABLE 1.1. Summary of Process Conditions

Run #	Temperature °C	Pressure atm	Feed Gas Composition mole %		Feed Gas Flow Rate cm^3/min
			CH_4	O_2	(NTP)
1	410	33.7	90.6	9.4	24
2	448	36.7	90.6	9.4	27
3	412	25.2	90.8	9.2	44
4	445	25.2	90.8	9.2	43
5	447	25.8	90.8	9.2	43
6	415	25.3	91.3	8.7	20
7	452	24.9	91.3	8.7	23
8	476	26.5	91.3	8.7	22
9	411	35.5	92.0	8.0	10
10	446	34.9	92.0	8.0	10
11	413	33.9	94.8	5.2	25
12	421	33.7	94.8	5.2	25
13	449	36.1	94.8	5.2	25
14	411	35.4	97.2	2.8	25
15	431	35.5	97.2	2.8	25
16	448	36.8	97.2	2.8	25

Table 1.2. Summary of Conversion and Selectivity Obtained During the Oxidation of Methane at Various Reaction Conditions.

Run #	Conversion (based on CH_4, mole%)	Selectivity, mole%			CH_3OH Yield, mole%
		CH_3OH	CO	CO_2	
1	3.9	16.4	74.3	9.3	0.64
2	1.8	17.0	69.8	13.2	0.31
3	3.6	13.2	70.1	16.7	0.48
4	5.0	43.2	56.8	vs	2.18
5	5.0	30.8	59.7	9.5	1.56
6	5.8	37.6	54.5	7.9	2.20
7	8.4	55.0	38.4	6.6	4.60
8	5.2	26.2	61.6	12.2	1.38
9	7.2	55.1	36.3	8.6	3.95
10	6.3	41.1	40.3	18.6	2.58
11	2.9	48.8	51.2	vs	1.41
12	4.3	57.4	37.1	4.9	2.50
13	2.4	42.9	57.1	vs	1.04
14	4.4	76.8	23.2	vs	3.38
15	4.3	76.8	23.2	vs	3.29
16	3.4	68.3	31.7	vs	2.32

TABLE 1.3. Characteristics of the Temperature Oscillations

Experiment #	Type of Oscillation	Frequency /min	Amplitude
1	relaxation	2	16
2	chaotic	10	--
3	relaxation	2	19
4	sharp	8	3
9	relaxation	0.5	8
10	irregular	3	3
12	relaxation and irregular	2-3	4
17	relaxation	1	8

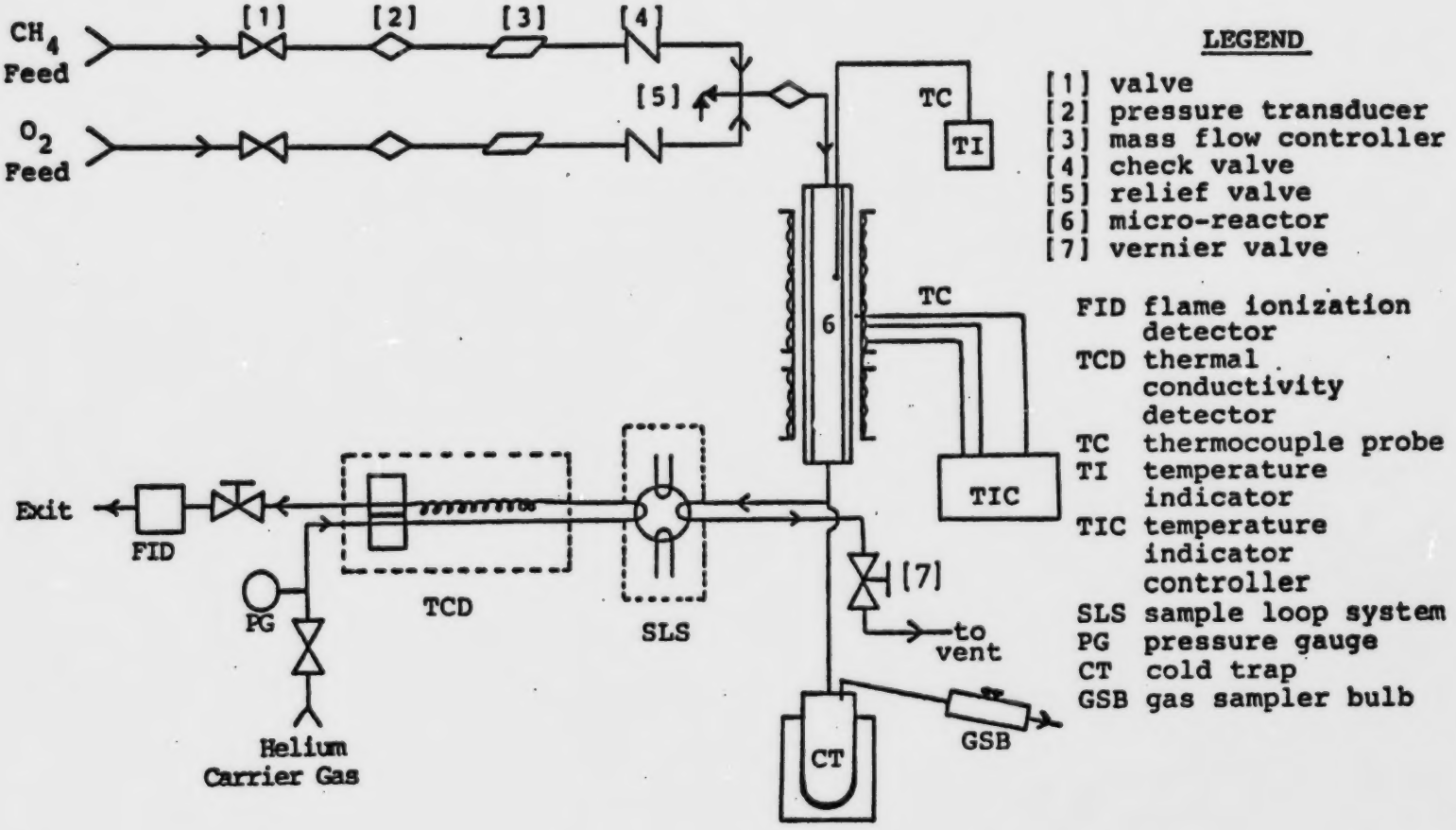


FIGURE 1.1 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL ASSEMBLY

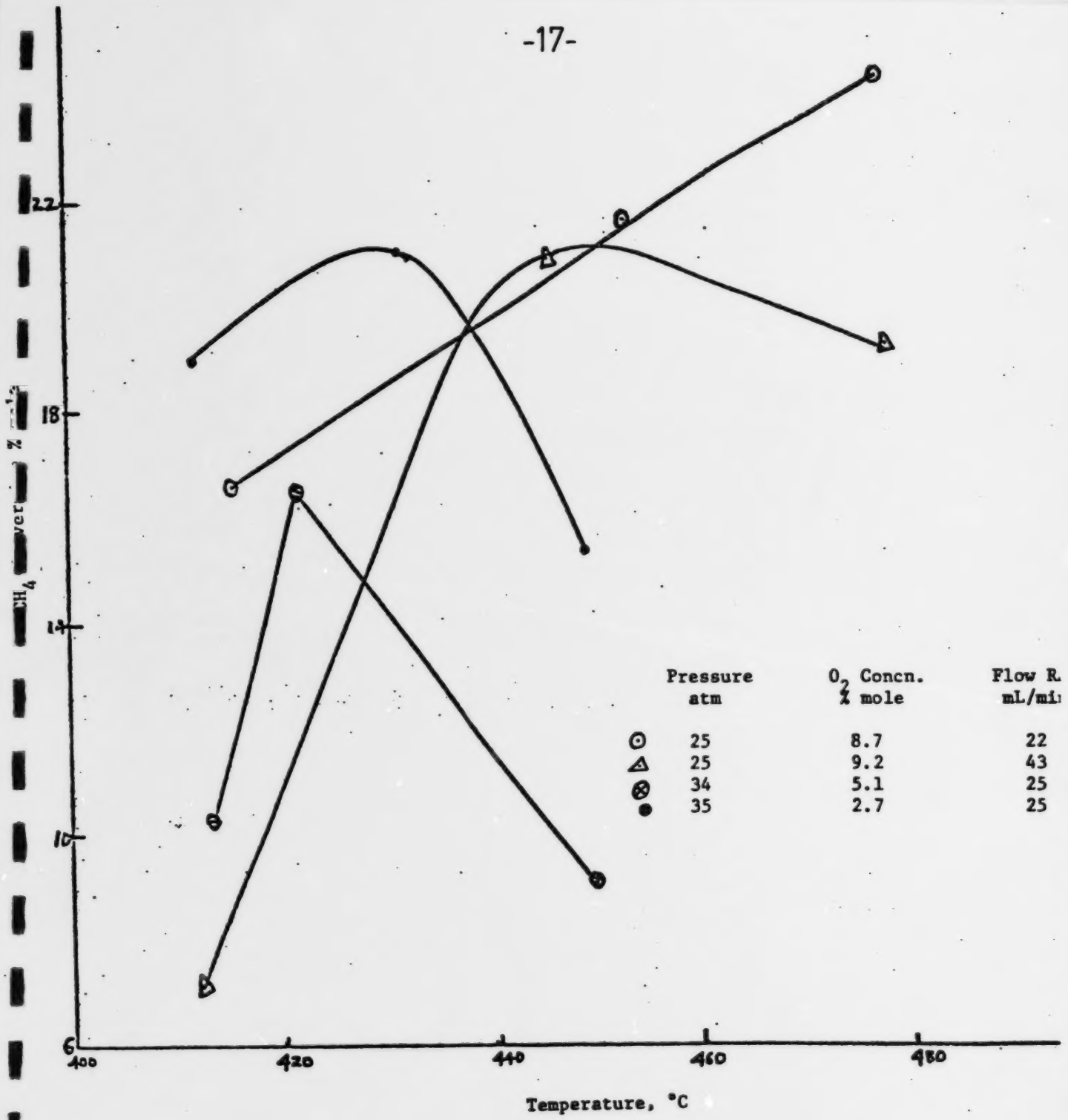


Fig. 1.2. Effect of reaction temperature on methane conversion.

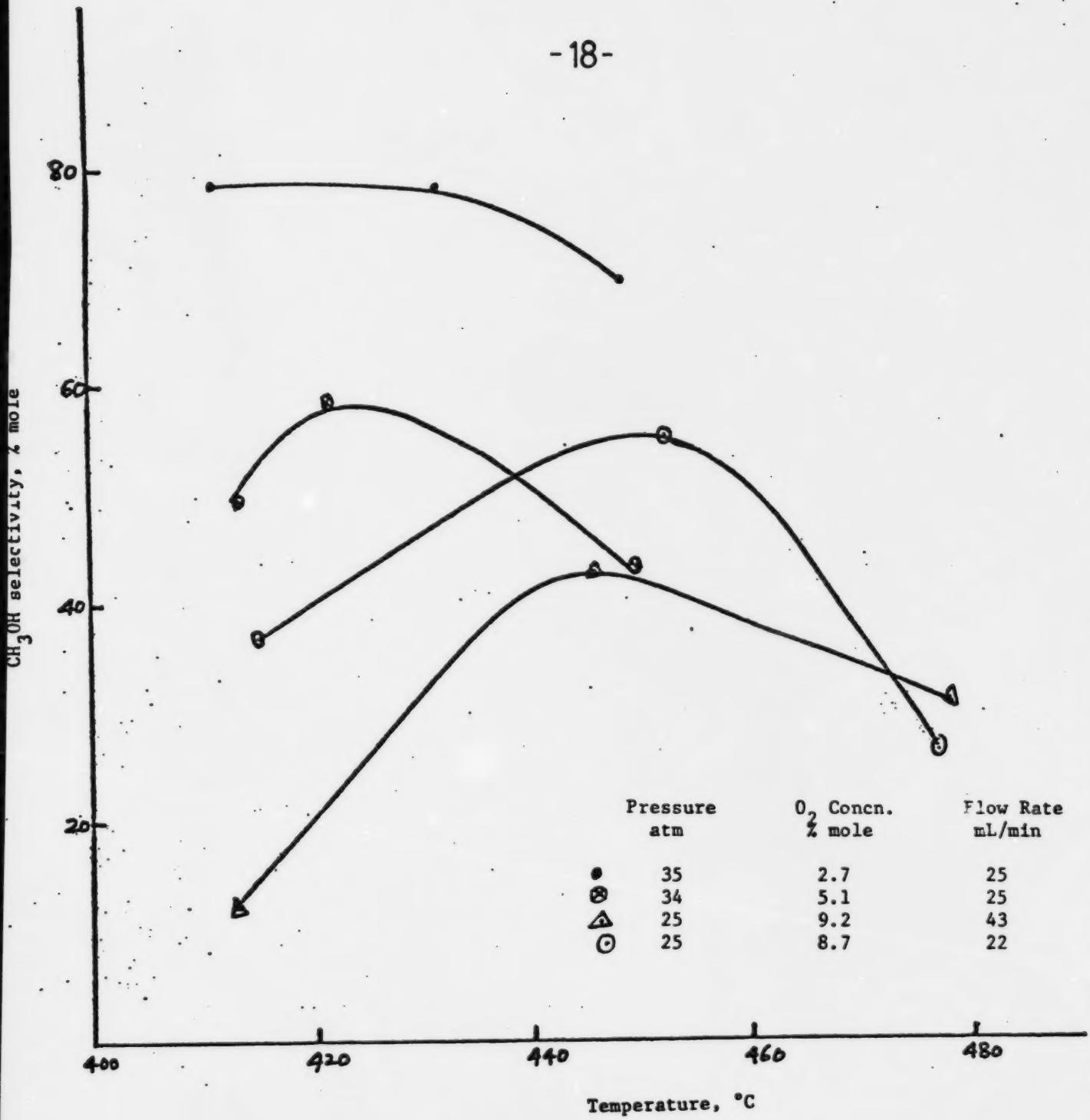


Fig. 1.3. Variation in methanol selectivity with reaction tempeature.

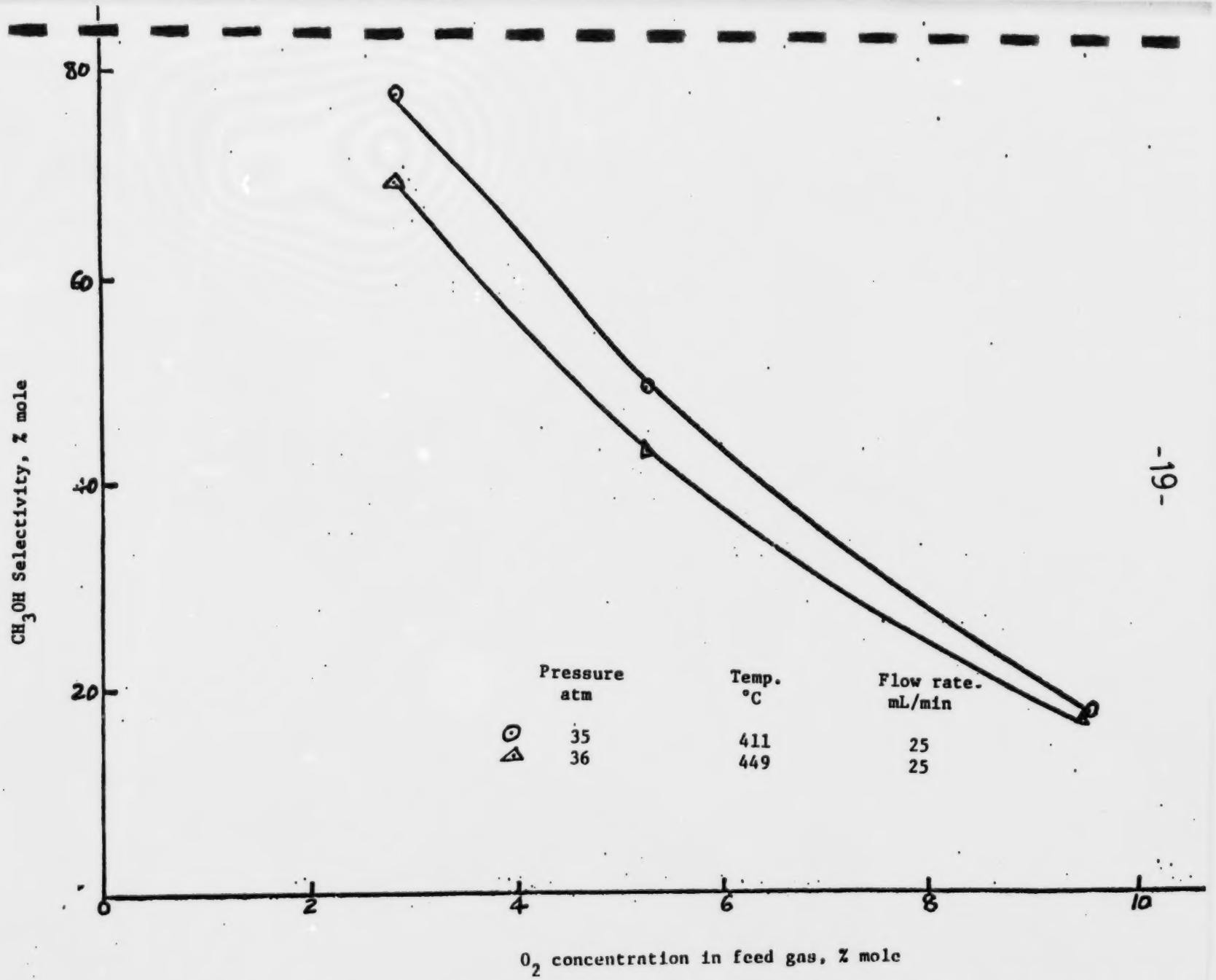


Fig. 1.4. Variation in methanol selectivity with oxygen concentration in the feed gas.

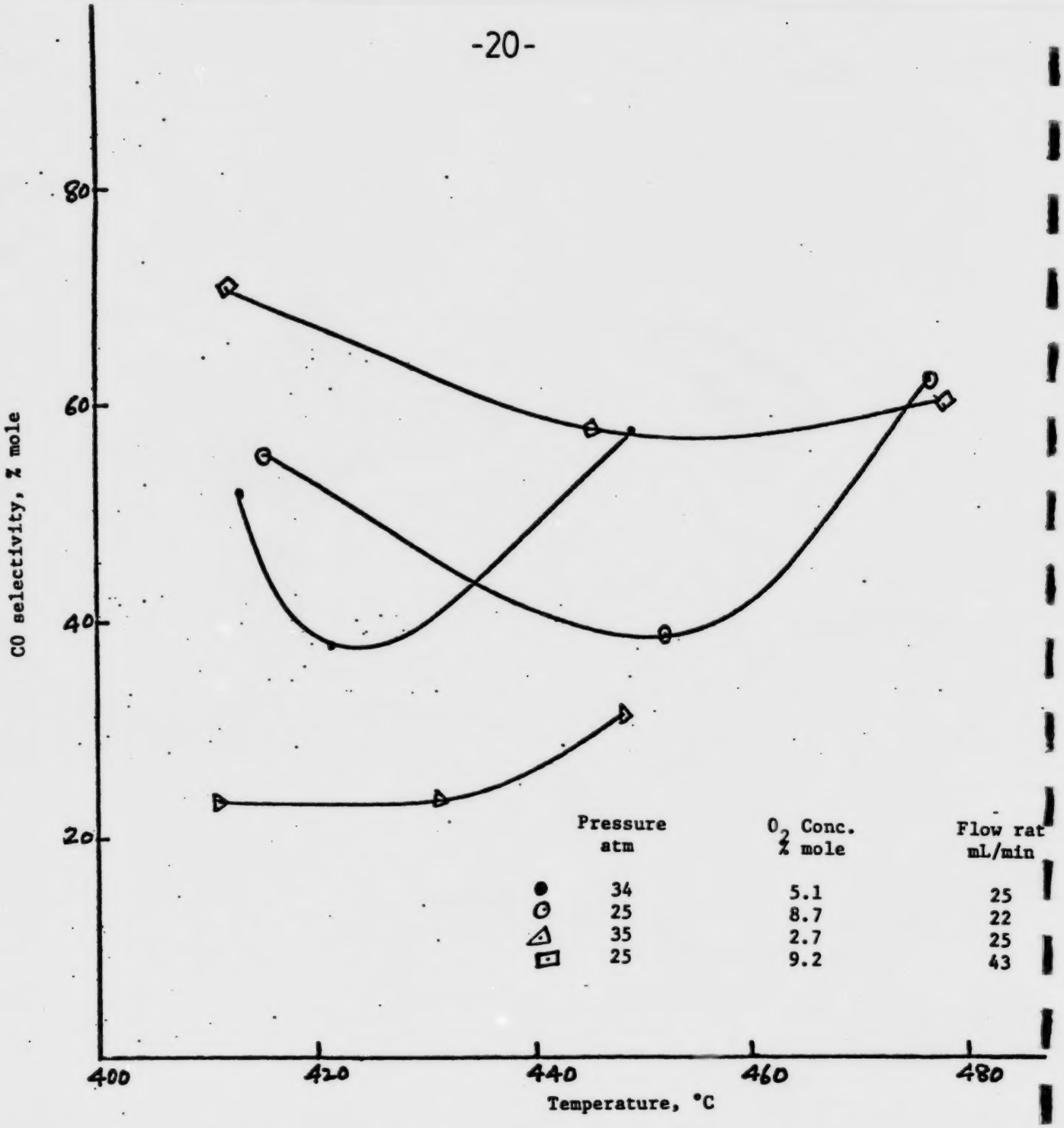


Fig. 1.5. Variation in CO selectivity with reaction temperature.

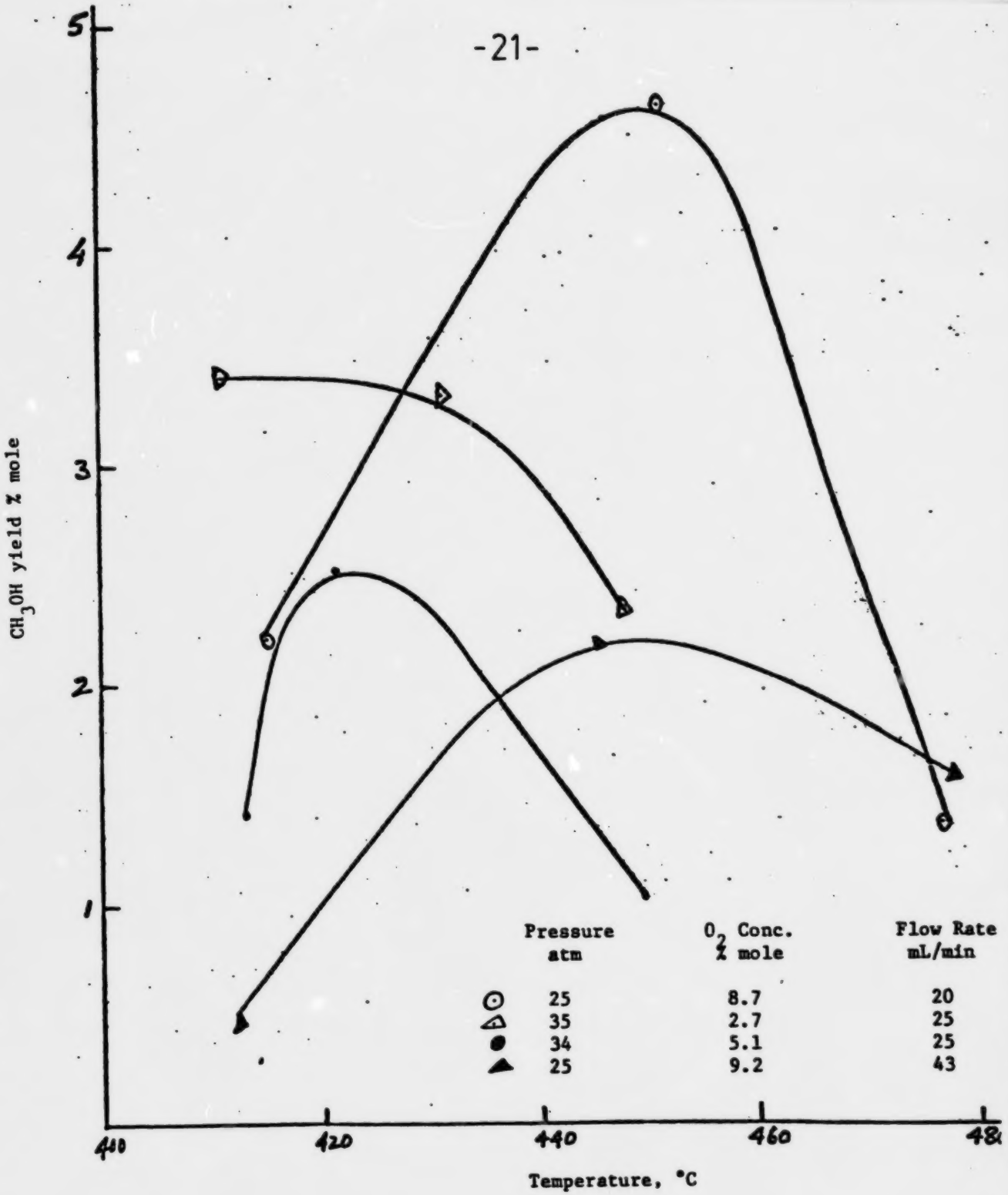


Fig. 1.6. Effect of reaction temperature on methanol yield.

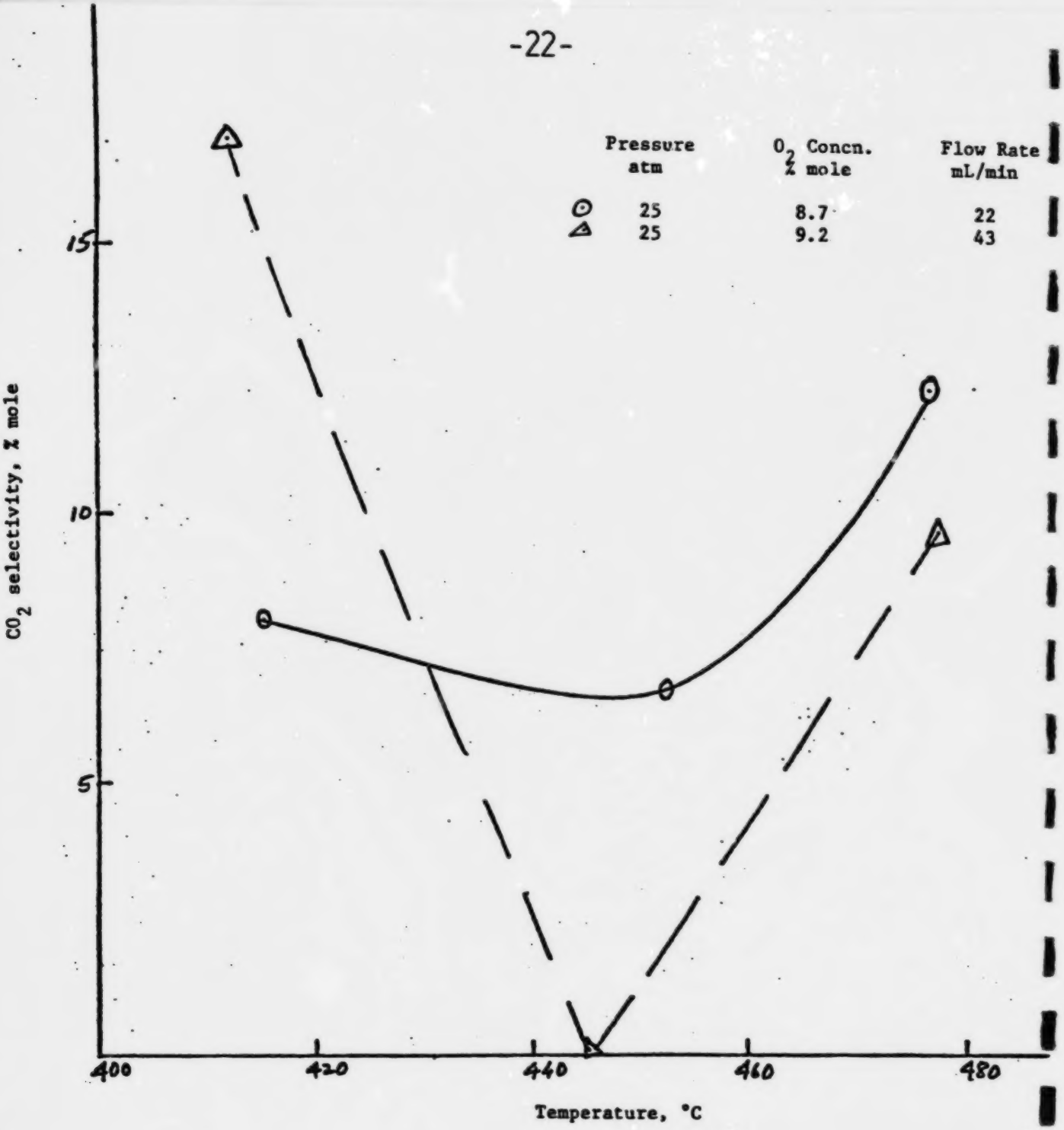


Fig. 1.7. Variation in CO_2 selectivity with reaction temperature.

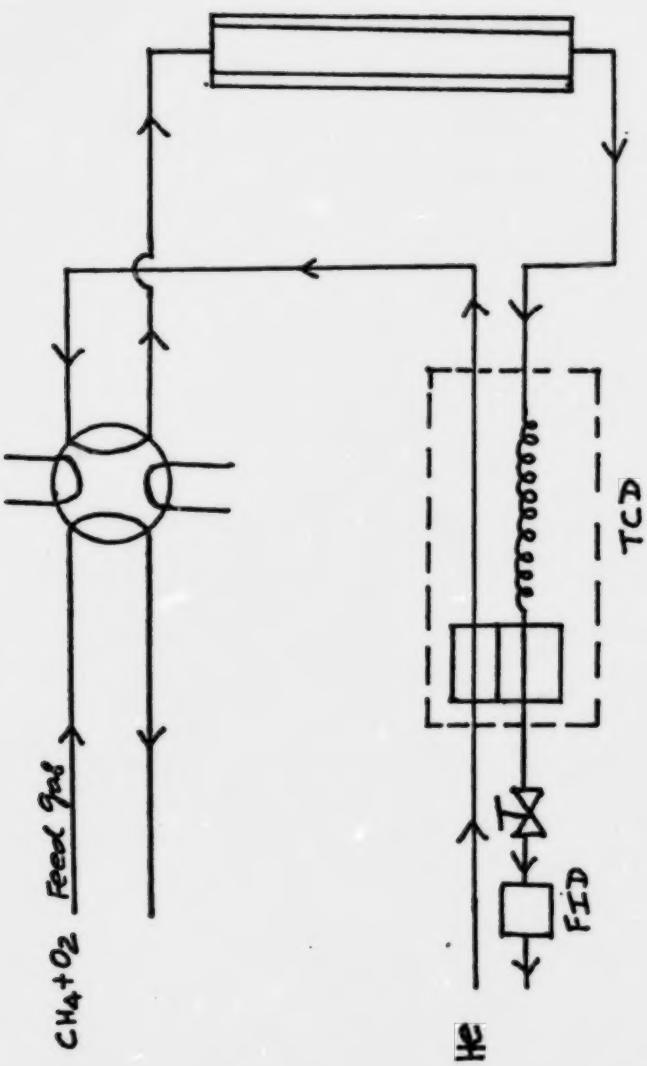


Fig. 1.6. Experimental set-up used in pulse flow studies.

PART TWO

Sensitization Initiation (Task 2) and Optimization (Task 3)

INTRODUCTION

This section describes the work carried out to evaluate the effect of homogeneous sensitizers on the methane to methanol oxidation reaction (Task 2). These sensitizers were selected on the basis of their ability to initiate the oxidation reaction (Appendix 2.I). Some of the more effective sensitizers were studied in more detail (Task 3).

Fifty runs in all were carried out to evaluate 31 sensitizers, operating under various experimental conditions, all in the large diameter (12.7 mm I.D.) glass lined reactor, and compared to the reaction process in their absence.

The 31 sensitizers studied can be grouped into 4 major classes and some with subgroups (Table 2.1) (with references see Table 2.2).

EXPERIMENTAL PROCEDURE

The reaction apparatus was modified to accept an 'initiator trap' (see Figure 2.1) and associated control lines which would permit the introduction of the sensitizer into either the methane or oxygen reactant gas streams. Provision was also made to allow the trap to be by-passed by using a 4-way switching valve (Whitey SS43YF2-4). In this way the oxidation reaction could be studied in the presence or absence of the chosen initiator.

The trap consisted of 6.3 cm o.d. x 34 cm length aluminum cylinder which had been bored out (1.3 cm x 28.5 cm) to accept a glass tube sealed at the lower end which would contain the sensitizer. This allowed the sensitizer to be weighed before and after an experiment and prevent possible reaction with the aluminum walls. Aluminum was chosen for the cylinder because it maintains its strength at low temperatures.

The gas chromatograph was modified to accept a Valco 10-way gas sampling valve to permit the use of a 2 column analytical system.

To obtain a reasonably stable reaction mixture the CH_4 and O_2 gas streams were allowed to run overnight and the composition monitored the following day.

The reactor temperature was set to 250°C (below Natural gas complete reaction temperature, 350°C) and the sensitizers introduced into the CH_4 gas stream (excepting peroxides) by means of the sensitizer trap.

The trap temperature was set according to the boiling point of the sensitizer, usually 30-50°C below T_b.

The reaction temperature was increased stepwise by increments of 25-50°C depending on the reaction velocity, as monitored by O_2 consumption, until all of the reactant O_2 was consumed or was close to completion.

The reaction temperature was then lowered to establish the minimum temperature for complete reaction (MTCR).

The oxygen concentration was varied between 5-10% to monitor the effect on product oxidized carbon selectivity and arbitrarily from sensitizer to sensitizer. The flow rate was maintained at 40-60 mL/min

NTP corresponding to a reactor flow rate of 8-12 mL/min at 10 atm and 600 K subject to experimental variation.

The gas chromatograph was calibrated with respect to some of the sensitizers used and a 10% squalane/chromosorb P (60-80 mesh) (W/W) was used to detect the higher hydrocarbons. The calibrations with respect to some of the liquid products were rechecked (see Table 2.II(i), Appendix 2.II).

RESULTS AND DISCUSSION

The results obtained in Runs 68, 72 and 77-115 have been summarized and presented in Table 2.3 since the data on which it is based is too cumbersome in its complete form. Selected results from the DTBP, IPA and CH_3CHO studies are included in this summary, with greater detail concerning Runs 68-76 being given under the appropriate headings.

Generally the summarised data refers to the product analysis corresponding to the MTCR. The values for conversion, methanol selectivity, formaldehyde selectivity where applicable, and carbon balance determinations are given.

The initial experimentation with Ditertiary Butyl Peroxide (DTBP) was concerned with (i) the detection of the decomposition products of DTBP and (ii) the optimum operating temperature.

Ditertiary Butyl Peroxide (DTBP) Runs 64-71

This was initially thought to be most promising and was the first sensitizer to be studied. To establish conducive reaction conditions it was investigated in greater detail.

The decomposition of DTBP could be followed by monitoring either the ethane or acetone concentration in the exit gas stream (Appendix 2.I).

In practice it proved more reliable to weigh the DTBP before and after an experiment and to determine its concentration in moles with respect to the number of moles of reactant gas that had passed through the reactor during that time.

DTBP was conveniently detected as C_2H_6 at higher concentrations in the exit gas stream.

In Run 64 ethane was detected at a level of 0.13% (mole basis) in a stream of pure N_2, following the decomposition of DTBP at 250°C with the trap at room temperature (22°C).

In Run 65 the DTBP was incorporated into the oxygen reactant gas stream, due to its oxidizing nature, which comprised 6% of the overall reactant mixture of O_2 in CH_4. However, C_2H_6 was not detected in the exit gas stream, presumably its concentration was below the level of detection.

It was clear that insufficient DTBP was being incorporated into the O_2 stream, at the 6% O_2 level, and therefore the DTBP trap was heated.

In Run 66 the oxygen concentration was established at 10%. The temperature of the DTBP trap was raised to 50°C. This corresponded to a DTBP concentration in the reactant gas stream, i.e. in the reactor, of 0.25% (moles DTBP/moles reactant gas mixture).

In qualitative terms methanol was detected at 350°C in the presence of DTBP and at 360°C there was a small but definite improvement in the methanol yield using DTBP compared to runs in its absence (Run 67).

In Run 68 the reaction pressure was reduced to 10 atm from 30 which allowed an increase in the oxygen concentration to 20% and hence a direct increase in DTBP concentration. The DTBP trap temperature was maintained at 62°C at an 0_2 level of 20%. This corresponded to a DTBP concentration of 0.5 (moles DTBP/moles reactant mixture).

Again methanol was detected at 350°C in the presence of DTBP but not its absence. A more quantitative measure of the sensitizers' effect was required.

At 390°C, in the presence of DTBP, 30% of the available reactant oxygen (20%) was consumed corresponding to an absolute 0_2 consumed concentration of 6%. This translated into a conversion of 2.6% and a methanol yield of 0.95% at 37% selectivity (Table 2.4).

At 390°C in the absence of DTBP (Run 69) the 0_2 consumption was 26% of that available (5.2% absolute). The conversion was 1.5%, methanol yield 0.9%, and selectivity a surprisingly high 62%, CO was not detected here (column switching error) and this probably accounts for an artificially high value of CH_3OH (Table 2.5).

At 400°C in the presence of DTBP oxygen was completely consumed, the conversion was 13%, the methanol yield 2.6% at a selectivity of 21% (Table 2.5). In the absence of DTBP only 83% of the available 0_2 was consumed (16.4% absolute) at 400°C. The conversion was 11.0% and methanol yield 2.8% at a selectivity of 26% (Table 2.4).

It was necessary to raise the reactor temperature to 410°C to consume all of the oxygen in the absence of DTBP where the conversion, yield of methanol and selectivity values are similar to those obtained in its presence at 400°C (Table 2.5).

Runs 70 and 71 were carried out at atmospheric pressure again incorporating DTBP into the oxygen stream. It was required, however, to raise the reaction temperature to around 480°C to obtain measurable reaction. The effect of the initiator at these temperatures was marginal and of no experimental significance.

It seemed from studies at 30, 10 and 1 atm that the 10 atm level was the most suitable for the initiator experiments.

It was argued that an abstractable hydrogen could possibly initiate the chain reaction with the resulting free radical reacting with O_2. Thus a secondary or tertiary hydrogen could be easily abstracted and some model compounds were selected to test this possibility (see Appendix 2.I).

Isopropyl Alcohol (IPA) Runs 72-74

The oxygen concentration was set at 12% and the initiator, being nonoxidizing, was introduced into the CH_4 stream at a concentration of 2.4% (moles IPA/moles reactant gas) and the trap heated to 51°C.

At 375°C in the presence of IPA, 22.5% of the available oxygen was consumed (2.6% absolute). 1.0% of the methane was converted corresponding to a methanol yield of 0.9% at a selectivity of 84% (Table 2.6).

The methanol selectivity was high as CO was not detected.

At 390°C some 60% of the available oxygen was consumed (7.0% absolute) improving the conversion to 3.0% and the methanol yield to 2.5% at 81% selectivity (Table 2.6).

In the absence of IPA at 390°C oxygen consumption fell to 44% of that available (5.1% absolute) returning a conversion of 2% and a methanol yield of 1.6% at a selectivity of 84% (Table 2.7).

All of the available oxygen was consumed at 400°C in the presence of IPA corresponding to a conversion of 4.4% and a methanol yield of 3.3% at a selectivity of 76% (Table 2.6).

Raising the IPA concentration to 5.6% increased the oxygen consumption and improved the conversion and methanol yields at both 375 and 390°C (Table 2.6).

Acetaldehyde Runs 75 and 76

Because of the low boiling point of acetaldehyde (21°C) it was necessary to cool the trap in a Dewar of ice. As with IPA the acetaldehyde was introduced into the CH_4 stream, at a concentration level of 9% (Run 76).

In Run 75 some methanol and water were detected at temperatures as low as 280°C but in small amounts. As the temperature was raised methanol was not detected, but a peak subsequently identified as acetic acid appeared. These analyses were carried out using a Chromosorb 102 column to elute the higher boiling components. In Run 76 Porapak T was reinstalled in place of Chromosorb 102 so that methanol could be more clearly identified.

Considerable reaction took place at 380°C, though seemingly an induction period of around 1 hour was required before the reaction rate reached a steady state.

The maximum conversion of CH_4 recorded at 380°C was 6.2% corresponding to a yield of 3.2% methanol at a selectivity of 52%.

Oxygen consumption was 57% of that available (6.3% absolute) (Table 2.8).

At 386°C the conversion improved to 7.7% with 85% of the available 0_2 being consumed (9.2% absolute) returning a methanol yield of 3.3% with selectivity falling slightly to 43%, Table 2.8.

The condensable fraction was collected from the reactor during Run 76.

Identified in the 'collectate' were formaldehyde, water, methanol and acetic acid (Table 2.9). (In the remaining Discussion all of the results referred to can be found in Table 2.3 unless otherwise indicated.)

Absence of Sensitizer, Runs 78, 79, 81, 83 and 86

The minimum temperature at which complete reaction (MTCR) occurred in the absence of a sensitizer was 410°C at an 0_2 concentration of around 10%. The maximum value for the methanol selectivity was 52% and the minimum value was 41%. Formaldehyde was generally not detected with the exception of Run 83 where selectivities of 20-30% were found most usually following a reduction in the reactor temperature.

The MTCR of 410°C, and a 41-52% methanol selectivity were the values to be improved upon in the study of sensitizers using pure methane at a 10% 0_2 concentration.

2,2,4-Trimethylpentane (224-TMP), Runs 77 and 80

The 224 TMP concentration in Run 77 was higher than that in Run 80 at 3.3% mole sensitizer/mole reactant gas and the 0_2 concentration was lower at 9.4%.

The higher TMP concentration afforded a MTCR value of 363° whereas at 335°C only 81% (8.3% 0_2 absolute) of the available 0_2 was consumed. The effectively lower 0_2 concentration returned a higher methanol selectivity of 46.1% compared to 26.3 at 9.4% in Run 77.

The selectivity in formaldehyde was 51.3% in Run 77 compared to only 5.4% in Run 80 accounting for the difference in methanol selectivity. In effect the carbon specific selectivities of formaldehyde and CH_3OH should be added since formaldehyde is a useful product. This means that the combined useful selectivity in methanol and formaldehyde was higher at the higher sensitizer concentration for complete 0_2 consumption.

2,3,4-Trimethylpentane (2,3,4-TMP), Runs 82 and 84

The carbon specific methanol selectivity was highest at the 2.1% 2,3,4-TMP concentration level (41.0%) compared to a value of 33.5% at 3.1% 2,3,4-TMP. Again, however, the formaldehyde was significantly increased at the higher sensitizer concentration giving a higher combined useful oxidized selectivity. A lower MTCR value was obtained at the higher 2,3,4-TMP concentration. The MTCR was lower for 2,2,4-TMP compared to 234 TMP though this may simply reflect the higher 0_2 concentration employed (9.4% for 2,2,4-TMP cf 11.0% for 2,3,4-TMP).

Comparison of the two isomers would seem to indicate that 2,2,4-TMP generally favors higher selectivity of useful products.

Toluene, Run 85

No significant improvement was afforded by the addition of toluene. The MTCR was reduced by 10°C compared to its absence, at a higher 0_2

concentration. The methanol selectivity was 45.1%, quite good for a 12.4% 0_2 concentration but not significant compared to that in its absence (Run 83) though at a lower 0_2 concentration of 10.6%.

3-methyl-1-butene (3M1B±), Runs 87-90

3M1B was the first sensitizer found to reduce the MTCR to below 300°C, lower than that found for natural gas. Accordingly it was studied in more detail by varying both its concentration (trap temperature) and the reactant 0_2 concentration.

The highest methanol selectivity (58.5%) was obtained at the lowest 3M1B concentration of 1.6%, with formaldehyde not being detected by G.C.

As the 3M1B± concentration was raised (up to 6.5%) the MTCR was reduced. At the highest level of 3M1B± studied (10.8%) the MTCR remained at 292°C. Formaldehyde was produced at all of the higher 3M1B± levels, at around 19% selectivity.

From these results it is projected that a concentration of 3.0% would afford reaction at 300°C, or a little under, and give a methanol selectivity of 50% at 5-6% 0_2.

Compared to the methanol selectivity values usually obtained at the 5-6% 0_2 level in the absence of sensitizers (70-80%) this value of 50% appears low. It would seem therefore that some of the sensitizer itself was undergoing oxidation to CO and CO_2 (carbon products). This problem represents the essential feature of this task: to obtain a sensitizer that will improve or maintain the methanol selectivity of 80% at 5% 0_2 whilst lowering the operating conditions and undergoing very little self oxidation, i.e. the ideal sensitizer should decompose relatively slowly

to provide initiation species such as methyl radicals that will sensitize the CH_4 and be relatively resistant to oxidation. This last condition is the most difficult to meet.

Pentane, Run 91

At a concentration of 4.5% the MTCR was established at 286°C. The methanol selectivity was low at 34.5% but coupled with the formaldehyde selectivity of 30.3 the combined useful carbon selectivity was fair (65%) at 5.4% O_2.

Hexane, Run 92

Hexane produced results very similar to pentane but probably for a lesser concentration than recorded since some was lost in transfer from the trap. Interestingly, at the lower flow rate studied (19 mL/min NTP) (Run 92(ii)) the formaldehyde selectivity was increased at the expense of the methanol value. At 41 mL/min NTP the methanol selectivity was good at 65.0% with no formaldehyde detected (Run 92(ii)) and in a yield of 5.6%. This result represented the sensitizer combining the highest methanol selectivity operating at the lowest reaction temperature (285°C). See Table 2.10.

Cyclohexane, Run 93

At a concentration of 1.9% cyclohexane proved more efficient than any previous sensitizer per mole, at reducing the MTCR though no lower than 286°C. Selectivity to methanol was lower however at 36.8% with the formaldehyde selectivity at 23% returning a lower combined useful product selectivity than pentane or hexane but comparable to 3M1B±.

Cyclohexene, Run 94

Formaldehyde was detected in the study of cyclohexene but only when O_2 was in excess, i.e. incomplete consumption. The methanol selectivity was low at 46% at an oxygen level of 5.0%. The major difference in this study and the previous four runs was that the MTCR was 100°C higher at 385°C.

Acetone, Run 95

The methanol selectivity was fairly good at 61% using an oxygen concentration of 7.7% but the MTCR was little reduced at 395°C from that of 410°C in the absence of a sensitizer.

Isopentane, Run 96

Isopentane compared well with pentane, excepting the higher concentration used, returning similar values for the methanol selectivity, MTCR and a combined useful oxidized product selectivity of 65%.

Benzene, Run 97

The MTCR and methanol selectivity results obtained for benzene were very similar to those for toluene. However, formaldehyde was additionally produced using benzene giving a high combined useful oxidized product selectivity (83.5%).

1-Pentene, Run 98

With oxygen in excess, formaldehyde was detected. The MTCR was

estimated at 330°C since the investigated temperature did not exceed 304°C with 75% of the available oxygen being consumed (absolute = 5%).

Isopropyl Ether (IPE), Run 99

The methanol yield was recorded as 56% at 7.4% oxygen and an MTCR of 347°C. Formaldehyde was not detected by G.C.

Diethyl Ether (DEE), Run 100

DEE provided the lowest MTCR value in this series of studies (225°C) at a concentration level of 4%. The methanol selectivity was disappointing however at 35%. Coupled with the formaldehyde selectivity of 22% the useful oxidized carbon product selectivity equalled 57%. This value was still lower than values recorded previously for other sensitizers suggesting that some of the DEE was being oxidized. The MTCR value of 225°C was significant however.

Ethanol, Run 101

Ethanol at 2.5% returned a value of 53% for the methanol selectivity and a formaldehyde selectivity of 12% at a high MTCR of 382°C.

Methanol, Run 102

It was interesting to speculate if the introduction of the reaction products into the reactor with the reactant would have any positive effect on the reaction overall. Accordingly methanol, formaldehyde and water were selected for this purpose.

The major product, following minimal reaction sensitization by methanol (MTCR = 386°C), was CO with a selectivity of 48%. The methanol selectivity was 40.4% after subtracting the initial methanol concentration in the reactant gas, at an oxygen level of 9%. This value is therefore approximate since it was impossible to determine what proportion of the reactant methanol was consumed.

This study supported the previously held assumption that methanol decomposes primarily to CO at higher temperatures.

Formaldehyde was detected at 400°C at a selectivity of 32% while the methanol selectivity dropped slightly to 39% but significantly the CO selectivity was reduced to 24%.

Formaldehyde Solution (36.5% W/W), Run 103

Formaldehyde was not detected at all in the product gas stream above the MTCR of 385°, similar to methanol in Run 102, and therefore was being completely consumed. The methanol yield was improved compared to Run 102 at 58.5%. The CO selectivity was 30.6%.

Cumene, Run 104

Similar to toluene and benzene (Runs 85 and 97), cumene did not improve the reaction situation significantly with the methanol selectivity values for these aromatic sensitizers being in the range of 45-50% at around the 5-12% oxygen level. As with toluene but not benzene, formaldehyde was not detected in the study of cumene.

Triethylamine (TEA), Run 105

TEA provided a methanol selectivity of 61.4% at a MTCR of 326°C. Some formaldehyde was produced at temperatures of 303°C and less, i.e. in the presence of oxygen.

Tetrahydrofuran (THF), Run 106

THF effected complete oxidation at 300°C but the CO_2 selectivity was high at 41.4% restricting the methanol selectivity to 39%. Formaldehyde was detected at 275°C.

Propanedithiol (PDT), Run 107

A methanol selectivity value of 61.8 was obtained in the presence of PDT though the MTCR was high at 383°C, but at a high O_2 concentration level (9%).

Cyclopentane, Run 108

The MTCR was significantly low at 246°C, second best to DEE, though the cyclopentane concentration was twice that of the DEE due to overheating of the sensitizer trap. Methanol selectivity was adequate (51%) at an O_2 concentration of 9%.

2,3-Dimethylbutane (2,3-DMB), Run 109

2,3-DMB returned the highest methanol selectivity (77%) at a reasonable MTCR of 322°C using an oxygen concentration of 10.4%. The methane conversion was lower than expected (7%). However CO_2 was not detected in any of the determinations. The reaction did not produce formaldehyde. Not all of the available DMB was consumed and it was estimated that the concentration consumed in the reaction was something

less than 3.0%. Essentially this compound sensitized the reactor such that the oxidation products were limited to methanol, CO and water. This was the most efficient compound in terms of producing methanol at high selectivity and low reaction temperature (Table 2.10).

2,3-Dimethylbutene (2,3-DM-2-B≠), Run 110

This sensitizer was less effective than 2,3-DMB in terms of the methanol selectivity (61%) and MTCR (360°C) at a lower oxygen concentration of 8% but better than many others. The conversion was again lower than expected. The value of 61.3% for the methanol selectivity was the highest recorded from the alkene class of sensitizers.

Water (H_2O), Runs 111 and 112

Water produced a methanol selectivity of 64% regardless of its concentration. Formaldehyde was not detected at all. The conversion at both concentrations was lower than expected based on the complete consumption of oxygen (7 and 8%). The MTCR was 400°C, and so marginally lower than in the absence of water.

2,3-Butanedione (Biacetyl), Run 113

The diketone biacetyl was less effective than acetone in terms of methanol selectivity (41%). The MTCR value was similar though the biacetyl concentration was about one fifth that of acetone.

Methanethiol (MT), Run 114

The methanol selectivity was 67% using an oxygen concentration of

4% but at a MTCR of 404°C.

Dimethyl Ether (DME), Run 115

The methanol selectivity was a very low 26% at an oxygen concentration level of 9%. The formaldehyde selectivity was 23% giving a combined useful oxidized product selectivity of 49% at a sensitizer concentration of less than 1% (lowest studied) at a MTCR of 310°C.

CONCLUSIONS

Of the four classes of compounds studied the hydrocarbons generally appear to be the most readily adapted to sensitization in reducing the MTCR below 410°C and increasing methanol selectivity above the 41-52% range, found in their absence in the oxidation reaction with O_2 at the 10% concentration level. Within this class, the alicyclic compounds best satisfied these criteria, with the 2,3-DMB sensitized oxidation reaction returning the highest methanol selectivity of 77% at 322°C and hexane effecting reaction at 286°C and a methanol selectivity of 65%. 2,3-DMB was considered superior to hexane because of the relatively higher methanol selectivity produced at a higher concentration of O_2.

In the oxygen-containing class of compounds DEE, in terms of MTCR, was the most effective sensitizer investigated overall.

Good methanol selectivity was obtained using TEA (61%) and further amines could be studied.

Use of the thiols indicated that sulphur did not have a detrimental or inhibitory effect on the oxidation reaction indeed PDT gave a methanol selectivity of 62% at 9% 0_2. The oxidation reaction was relatively unassisted by the remaining oxygen-containing subgroups of alcohols, ketones, aldehydes, formaldehyde and water. 2,3-DMB returned the highest methanol selectivity at 77% followed by methanethiol, hexane and water (see Table 2.10).

A feature of this study was the production of formaldehyde, generally favored when the reaction was sensitized. (Experimental parameters favoring formaldehyde included lower reactant flow rates, lower reaction temperatures and the presence of oxygen).

The formaldehyde selectivity was highest in the presence of 2,2,4-TMP, benzene, hexane (low flow rate) and 3-methyl-1-butene (all above 30%) (see Table 2.10).

The largest combined methanol-formaldehyde selectivity value was observed in the presence of benzene (83.5%) followed by 2,2,4-TMP.

An attempt to determine the relative efficiency of the sensitizers investigated in this study has been made in Table 2.11. In Table 2.11i) the sensitizers effecting the lowest MTCR combined with the highest methanol selectivity are listed in order. In Table 2.11ii) a similar exercise was carried out combining the lowest values of MTCR with the highest combined methanol-formaldehyde selectivity. No attempt was made to allow for sensitizer or oxygen concentration.

Comparison of the two tables shows that the most efficient sensitizers in terms of producing methanol/useful oxidized product at minimum reaction temperatures include hexane, 2,3-DMB and 3M1B$\clubsuit$. The appearance of hexane in both tables can be explained in terms of flow

rate. At the lower flow rate investigated formaldehyde was produced, which coupled with methanol, gave a high combined selectivity. For the higher flow rate formaldehyde was not detected and methanol alone in good selectivity was produced. 2,3-DMB is the most efficient in both tables because of the high methanol selectivity returned in its presence, albeit at a higher MTCR.

Interpretation of the efficiency of these sensitizers, in terms of the number of active hydrogen atoms they possess and the ratio of the relative rate constants per active H atom, is not straightforward (Table 2.12). The data would seem to indicate that relatively few active H atoms are required together with an intermediate relative rate constant value. However, this does not explain why 2,3-DMB should be more efficient than IPE. Another exception is 3M1B$_4$ which is fairly efficient with one active hydrogen and a high relative rate constant value, unless a compensation effect exists 'between' these parameters.

There is no doubt that some of the compounds tested did in fact significantly sensitize the reaction either by lowering the reaction temperature or affecting the selectivity towards methanol.

However, the large amounts that were added in this study, and their consumption in the reaction adds to the cost of the system and so becomes commercially unacceptable.

One approach to sensitization which may be considered, and which would not add significantly to the cost of the system, is to leave traces of C_2, C_3 and C_4 hydrocarbons in the stripped natural gas. This would require a more detailed evaluation.

FUTURE WORK

Any study to determine the "best sensitizer" will have to include an estimation of the degree to which the sensitizer itself is oxidized. This is an important factor in determining the most efficient sensitizer.

Table 2.1. Classes and subgroups of sensitizers

1.	Hydrocarbons	
	i) Saturated, alicyclic:	2,2,4-TMP, 2,3,4-TMP, pentane, isopentane hexane, 2,3-DMB
	ii) Unsaturated, alicyclic:	2,3-DM-2-B±, 3M1B±, 1-pentene
	iii) Cyclic:	cyclopentane, cyclohexane, cyclohexene
	iv) Aromatics:	benzene, toluene, cumene
2.	Oxygen containing compounds	
	i) Ethers:	DEE, DME, IPE, THF
	ii) Alcohols:	IPA, ethanol, methanol
	iii) Ketones:	acetone, biacetyl
	iv) Aldehydes:	acetaldehyde, HCHO
	v) Misc.	water, DTBP
3.	Sulphur containing compounds	
	i) thiols:	PDT, methane
4.	Amines:	TEA

Table 2.2. Boiling points and references to sensitizers studied in Task 2.

Compound	Run No.	Boiling Point (°C)	Reference
DTBP	66,68,70	111	1,2,11
IPA	72,74	82.4	1
CH_3CHO	75,76	20.5	1,7
2,2,4-TMP	77,80	98.5	1
2,3,4-TMP	82,84	113.5	1
$C_6H_5CH_3$	85	111	1,3,4,5
3M1B	87-90	20	1
nC_5H_{12}	91	35.5	1
nC_6H_{14}	92	69	1
cC_6H_{12}	93	81	1
$1\text{-}C_5H_{10}$	98	30	1
cC_6H_{10}	94	83	1
C_6H_6	97	79	1
C_2H_5OH	101	78.8	1
CH_3COCH_3	95	55.5	1,3,8,9
cC_5H_{10}	98	50	1
2,3-DMB	109	58	1
2,3-DM2B	110	73	1
iC_5H_{12}	96	28	
DME	115	-25	1,3,6
DEE	100	34.6	12
IPE	99	35.4	1
THF	106	65	1
$C_6H_5C_3H_7$	104	153	1

Table 2.2...cont'd...

Compound	Run No.	Boiling Point (°C)	Reference
Biacetyl	113	88	1,10
MT	114	7.6	
PDT	115	169	
CH_3OH	102	64.6	1,3,6
HCHO(Solu)	103		
H_2O	111,112	100	1
TEA	105	89.5	1

Table 2.3. Summary of Reaction data: The sensitized oxidation of methane.

Experimental conditions: Reactor Pressure = 10 atm Reactor Flow Rate = 40 - 80 mL/min (NTP)

Reactor Space Time = 292 - 180 s

Run#	Sensitizer	%[Sensitizer] (moles/mole CH_4)	Sensitizer Temp °C	%[O_2]	MTCR°C	%Conv. CH_4	%Yield CH_3OH	CH_3OH % Selectivity	HCHO % Selectivity	Σ CH_3OH-HCHO Selectivity	%Cbal.	%O_2 bal
68	DTBP	0.48	62	19.86	400	12.74	2.64	20.73	ND	20.73	104.6	92.10
72	IPA	2.40	53	11.53	400	4.42	3.35	75.88	ND	75.88	104.5	92.40
76	Acetaldehyde	9.10	-1	9.34	386	8.26	3.31	40.10	7.62	47.82	33.77	107.2
77	224 TMP	3.33	52	9.40	363	13.60	3.57	26.30	51.29	77.59	106.54	155.18
78	none	-	-	10.54	380	8.74	3.56	41.07	ND	41.07	105.5	134.5
79	none	-	-	9.52	410	7.01	3.05	43.52	ND	43.52	96.0	115.0
80	224 TMP	2.11	40	10.23	-	7.54	3.47	46.10	5.44	51.54	103.2	101.2
81	none	-	-	9.52	410	6.47	3.38	52.16	ND	52.16	98.55	127.4
82	234 TMP	2.07	48	9.82	-	10.87	4.45	41.00	small	41.00	107.7	135.4
83	none	-	-	10.65	410	10.00	4.65	46.0		46.60	107.40	120.2
84	234 TMP	3.10	57.5	11.00	371	13.71	4.60	33.47	19.10	52.57	98.10	138.6
85	Toluene	2.07	62	12.42	400	8.63	3.89	45.08	ND	45.08	112.12	101.0
86	none	-	-	10.05	400	9.02	3.79	41.97	2.63	44.60	101.90	117.9
87	3M1B±	6.55	-1.0	10.37	285	12.08	4.73	39.14	18.11	57.25	112.96	135.1
88	3M1B±	4.91	-1.5	10.92	292	11.97	4.05	33.80	19.78	55.38	108.11	112.8
89	3M1B±	10.80	-1.5	6.60	291.5	6.61	2.85	44.49	19.70	64.19	100.83	102.2

Expt'l Conditions Reaction Temp(°C)/Flow Rate (NTP)	Comments
	CH_3OH selectivity low due to high $[O_2]$ to incorporate sufficient DTBP
	CO not detected in any determination.
	Frac. O_2 consumed = 0.85 (= 9.34%) MTCR estimated at 400°C.
	low value for min Rxn temp. suggests some TMP in system
400°	Small amount of O_2 unconsumed. Frac. consumed = 0.90
355°	cf Run 77. Frac. O_2 consumed = 81% = 8.28% O_2
400°	Frac. O_2 consumed = 0.95 (= 9.0%)
375°	Frac. O_2 consumed = 0.93 HCHO yield generally small when detected except at 345°C (lowest temp) dominant product
	HCHO detected most often following a reduction in the reactor temperature % selectivity in such cases = 20-30%
	HCHO usually detected
	HCHO detected in all determinations Min. Rxn temp. determined from decreasing reactor temperature.
	" " " " " Min. Rxn temp. determined from increasing reactor temperature.
	3M1B± concentration higher in CH_4 stream at -1.5°C due to decrease in O_2 conc.

Run#	Sensitizer	%[Sensitizer] (moles/mole CH_4)	Sensitizer Temp. °C	%[O_2]	MTCR°C	%Conv. CH_4	%Yield CH_3OH	CH_3OH % Selectivity	HCHO % Selectivity	ΣCH_3OH-HCHO Selectivity	%CBal.	$\%O_2$ bal
90	3M1B±	1.56	-28	5.19	321	5.98	3.50	58.53	ND	58.53	102.75	153.35
91	C_5H_{12}	4.52	-1.0	4.4	286	10.26	3.55	34.55	30.33	64.88	101.20	153.35
92(i)	C_6H_{14}	5.40	25	5.40	285	8.60	5.60	65.00	ND	65.00	88.20	206.00
92(ii)	C_6H_{14}	5.40	25	5.40	285	13.76	4.90	35.33	32.90	99.23	105.40	258.41
93	cC_6H_{12}	1.87	26	5.19	286.5	6.05	2.22	36.77	22.25	59.02	97.62	151.60
94	cC_6H_{10}	1.00	23	5.0est	385	7.85	3.65	46.45	ND	46.45	92.74	156.6
95	Acetone	3.38	22	7.68	395	8.00	4.85	60.67	ND	60.67	112.6	171.8
96	iC_5H_{12}	4.56	0	5.22	286	12.25	5.16	42.10	22.73	64.83	116.10	264.9
97	C_6H_6	2.60	23	9.12	402	6.91	3.27	47.38	36.10	83.48	104.11	96.4
98	$1\text{-}C_5H_{10}$	3.18	0	6.56est	330	9.02	3.17	35.14	22.90	58.04	109.4	164.6
99	IPE	5.07	22	7.40	347	10.51	5.85	55.66	ND	55.66	104.0	199.5
100	DEE	3.90	0	4.61	225	9.56	3.33	34.82	21.60	56.42	94.31	177.0
101	C_2H_5OH	2.47	23	6.94	382	7.83	4.13	52.75	11.92	64.67	105.05	134.4
102	CH_3OH	1.86	23	9.22	386	7.70	3.11	40.40	-	40.40	94.45	148.4
103	HCHO solu.	1.26	59	7.21	385	6.43	3.50	58.55	ND	58.55	96.77	146.0
104	Cumene	0.62	80	8.45	400	7.26	3.60	49.42	-	49.42	96.0	149.0
105	TEA	7.01	54	6.28	326	6.26	3.84	61.37	-	61.37	100.30	139.0
106	THF	2.84	23	9.30	300	15.32	5.93	38.71	-	38.71	95.55	154.5
107	PDT	1.10	60	9.22	383	11.43	7.06	61.80	-	61.80	105.40	170.0
108	cC_5H_{10}	8.83	50	8.32	246	10.81	5.52	51.08	-	51.08	101.42	171.4

Expt'l Conditions Reaction Temp(°C)/Flow Rate (NTP)	Comments
	HCHO not detected at all. Low conc. 3M1B caused increased in min. Rxn temp.
	HCHO detected in all determinations. Rxn temp. did not exceed 350°C.
305°, 41 mL/min	HCHO not detected. HCHO favoured by temp. reduction and lower flows high.
285°, 19 mL/min	HCHO only detected at 280-285°C. Conversion value high.
	Min. Rxn temp. of 286.5°C obtained using sensitizer conc. of 2%.
	$[O_2]$ varied throughout experiment. Experiment at 5%.
	When reduction temp. reduced to 385, methanol selectivity decreased to 46.4 % with all O_2 consumed. Conversion high
	Significant HCHO selectivity. Compare with toluene (Run 85)
304°	Frac. O_2 consumed = 0.75
	HCHO not detected
	Lowest min. Rxn temp. recorded
	Carbon selectivity of CO high at 48%. HCHO formed at 400°C.
	HCHO all consumed; CH_3OH selectivity improved over Run 102. CO selectivity = 30%.
	HCHO only detected in 1 determination at 385°C following increase of reactor temp.
	HCHO produced as reaction temp. increased up to 303°C.
	HCHO detected at low level at 275°C. CO_2 selectivity high at 41.45%.
	HCHO detected initially at 385°C but consumed with time.
	Cyclopentane conc. high since heater mistakenly set at 50°C instead of 23°C HCHO detected in some determinations.

Run#	Sensitizer	Sensitizer Temp. °C	%[Sensitizer] (moles/mole	%[O_2]	MTCR°C	%Conv. CH_4	%Yield CH_3OH	CH_3OH % Selectivity	HCHO % Selectivity	Σ CH_3OH-HCHO Selectivity	%CBal.	%O_2 bal
109	2,3-DMB	23	3.44	10.37	322	6.68	5.12	76.60	-	76.60	113.60	133.33
110	2,3-DM2B	22	2.42	7.84	360	5.42	3.33	61.33	ND	61.33	107.60	107.24
111	H_2O	67	5.20	7.21	402	4.80	3.08	64.19	ND	64.19	92.43	105.30
112	H_2O	35	10.20	7.90	400	4.46	2.84	63.77	ND	63.77	95.44	124.15
113	Biacetyl	23	0.76	7.87	390	7.70	3.16	41.10	-	46.10	109.22	157.50
114	MT	-36	3.17	3.93	404	4.68	3.13	66.80	ND	66.80	102.30	148.81
115	DME	-60	0.85	8.74	310	7.41	1.93	26.09	22.95	49.04	96.40	118.75

Expt'l Conditions Reaction Temp(°C)/Flow Rate (NTP)	Comments
	Conversion low. Detection of 2,3-DMB in product CO_2 not detected in any determinations. Estimate consumed 2,3-DMB at 3.07%
	Conversion lower than expected. Probably due to O_2 consumption by sensitizer
	Conversion lower than expected.
	Conversion lower than expected.
	HCHO initially produced at 350°C.
	HCHO not detected.
	Selectivity towards methanol low, sensitizer conc. 1.0%.

Table 2.4. Oxidation of CH_4 in the presence of DTBP.

Run 68.

Pressure = 10 atm Initial oxygen concentration = 19.9%

Conc. DTBP = 0.50% (moles DTBP/moles reactant gas)

Temperature (°C)	Fraction O_2 Consumed (Absolute %)	% Conversion CH_4	% Yield CH_3OH	% Selectivity CH_3OH
390	0.30 (5.92)	2.62	0.95	36.42
400	1.00 (19.86)	12.74	2.64	20.73

Table 2.5. Oxidation of CH_4 in the absence of DTBP (Experimental conditions as Table 2.4).

Run 69.

400	0.83 (16.40)	11.0	2.82	25.67
410	1.00 (19.9)	12.56	2.66	21.17

Table 2.6. Summary of oxidation of CH_4 in the presence of IPA.

Run 72.

Pressure = 10 atm Initial oxygen concentration = 11.53%

Conc. IPA = 2.40% (moles IPA/moles reactant gas)

Temperature (°C)	Fraction O_2 Consumed (Absolute %)	% Conversion CH_4	% Yield CH_3OH	% Selectivity CH_3OH
375	0.225 (2.60)	1.04	0.873	83.92
390	0.60 (6.92)	3.04	2.47	81.20
400	1.00 (11.53)	4.42	3.35	75.88

Run 74.

Conc. IPA = 5.60% (moles IPA/moles reactant gas)

375	0.28 (3.27)	1.40	1.24	88.90
390	0.83 (9.52)	3.81	3.10	81.36

Table 2.7. Oxidation of CH_4 in the absence of IPA

Run 73.

390	0.44 (5.08)	1.95	1.64	84.24

Table 2.8. Summary of oxidation of CH_4 in the presence of Acetaldehyde.

Run 76.

Pressure = 10 atm Initial oxygen concentration = 11.0%

Acetaldehyde conc. = 9.1% (moles CH_3CHO/moles reactant gas)

Temperature (°C)	Fraction O_2 consumed (Absolute %)	%Conversion CH_4	%Yield CH_3OH	%Selectivity HCHO	%Selectivity CH_3OH
380	0.57 (6.3)	6.24	3.20	-	52.02
386	0.85	8.26	3.31	7.62	40.10

Table 2.9. Analysis of collected liquid fraction.

Run 76.

Column = Chromosorb 102 Initial Temp. = 110°C

Rise = 40°C/min

Hold at 150°C until CH_3OH eluted then 40°C/min to 200°C final

Compound	H_2O	HCHO	CH_3OH	CH_3COOH
Rt/s	114	162	226	544
Area	15908	792	4888	2317
Corr. A		394*	3442	1158*
mole %	67.67	1.68	14.64	4.93

*approximate

Table 2.10. Ranking of sensitizers in terms of (i) lowest MTCR; (ii) highest methanol selectivity; (iii) highest HCHO selectivity; (iv) highest combined methanol-HCHO selectivity.

	MTCR °C		% CH_3OH Selectivity		% HCHO Selectivity		Combined CH_3OH-HCHO % Selectivity	
1	DEE	(225)	2,3-DMB	(76.60)	224 TMP	(51.29)	C_6H_6	(83.48)
2	cC_5H_{10}	(246)	MT	(66.80)	C_6H_6	(36.10)	224 TMP	(77.59)
3	nC_5H_{12}, iC_5H_{12} 3M1B±, C_6H_{14}, cC_6H_{12}	(286)	C_6H_{14}	(65.00)	C_6H_{14}	(32.90)	2,3-DMB	(76.60)
4	THF	(300)	H_2O	(64.19)	C_2H_{12}	(30.33)	C_6H_{14}	(68.23)
5	DME	(310)	PDT	(61.80)	DME	(22.95)	MT	(66.80)
6	2,3-DMB	(322)	TEA	(61.37)	$1\text{-}C_5H_{10}$	(22.90)	nC_5H_{12}	(64.88)
7	TEA	(326)	2,3-DM2B±	(61.33)	iC_5H_{12}	(22.73)	iC_5H_{12}	(64.83)
8	$1\text{-}C_5H_{10}$	(330)	Acetone	(60.67)	cC_6H_{12})	(22.25)	C_2H_5OH	(66.67)
9	IPE	(347)	HCHO solu.	(58.55)	DEE	(21.60)	3M1B± H_2O	(64.19)
10	2,3-DM2B±	(360)	3M1B±	(58.53)	3M1B±	(19.78)	PDT	(61.80)
11	224-TMP	(363)	IPE	(55.66)	234 TMP	(19.10)	Cumene	(61.37)

*41 mL/min Reactor Flow Rate (NTP)

**19 mL/min " " " "

Table 2.11. Relative sensitizer efficiency

i) Order of sensitizers favouring low MTCR and high methanol selectivity

1. Hexane*
2. 2,3-DMB
3. 3-M1B±
4. TEA
5. 2,3-DM2B±
6. IPE

*(41 ml/min (NTP) flow rate)

ii) Order of sensitizers favouring low MTCR and high combined methanol-HCHO selectivity

1. Hexane**
2. 2,3-DMB+
3. 3M1B±
4. Isopentane
5. 224-TMP

**(19 mL/min (NTP) flow rate)

+HCHO selectivity = 0

Table 2.12. The abstraction of hdyrogen atoms by methyl radicals from the photolysis of acetone (for best sensitizers) (Trotman-Dickenson and Steacie)[+]

Compound	No. of Active Hydrogens	$k/k^{\frac{1}{2}} \times 10^{13*}$ at 182°C per active hydrogen
hexane	6	-
pentane	5	
2,3-DMB	2	36
3M1B±	1	102
TEA	9	9.5
2,3-DM2B±	12	12
IPE	2	36
224 TMP	3	20[+]

[+]assume similar to 234-TMP

*units of k = molecules, cm^3 seconds

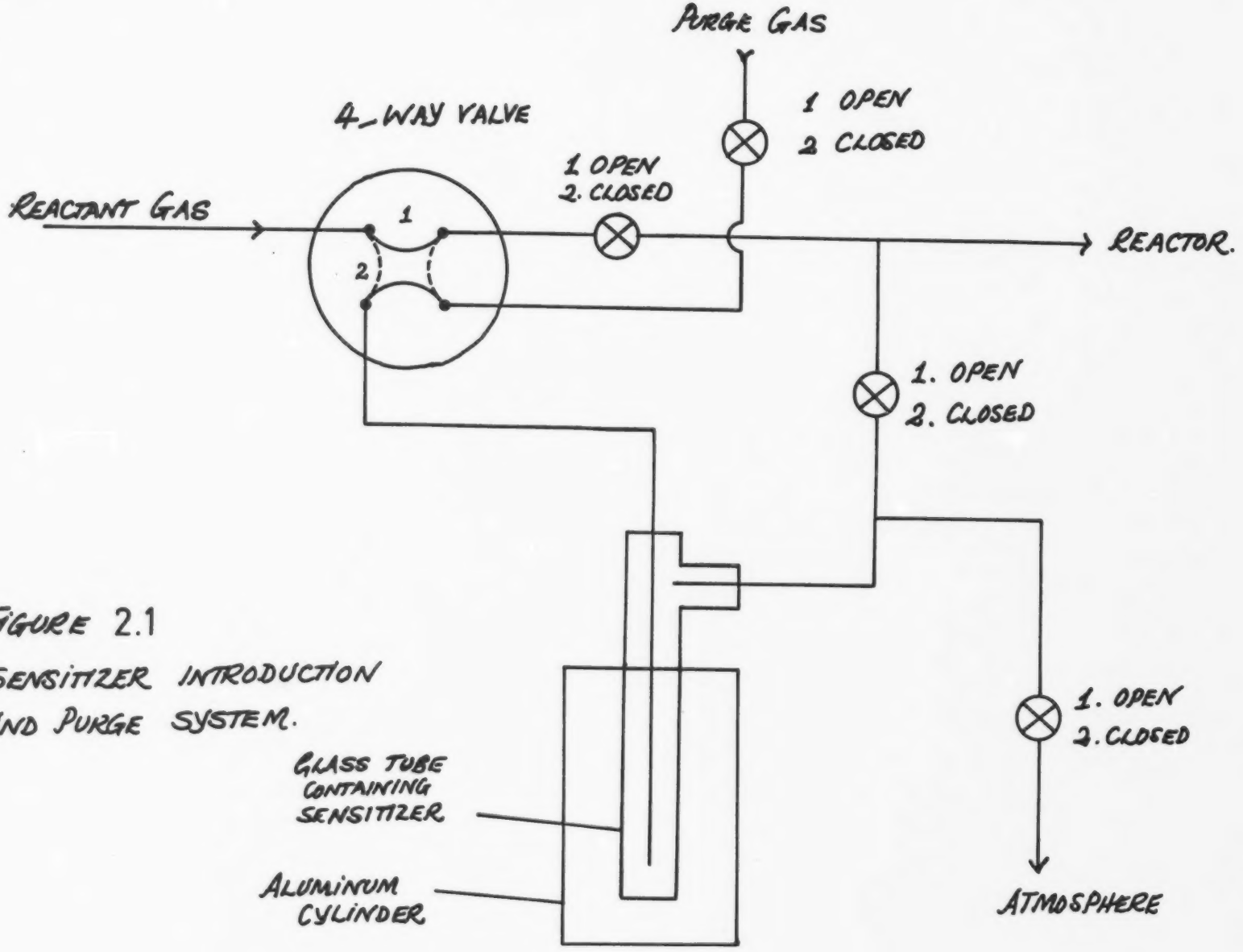


FIGURE 2.1

SENSITIZER INTRODUCTION AND PURGE SYSTEM.

APPENDIX 2.I

1. Di-tertiarybutylperoxide (DTBP)

The decomposition of this compound is well known[2]. It decomposes in the vapour phase as follows

$$(CH_3)_2COOC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3CO \qquad (1)$$

$$(CH_3)_3CO \xrightarrow{k_2} (CH_3)_2CO + CH_3 \qquad (2)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6$$

DTBP would seem to offer a good source of methyl radicals (see Table I of appendix 2.1.

2. Isoproyl Alcohol (IPA)

IPA was selected on the basis of its relatively higher rate of hydrogen abstraction[1] (i.e., loss of active hydrogen to medium; see Table I, Appendix 2-I.).

3. Acetaldehyde

Acetaldehyde is readily decomposed and according to the Rice-Herzfield mechanism[1] provides a ready source of methyl and acetyl radicals. Acetaldehyde is itself oxidized by oxygen and as such, as well as for reasons of increased concentration, it was introduced into the CH_4 stream.

It was felt that acetaldehyde would be incorporated into the reaction mixture at a significant concentration due to its low boiling point. The methyl radical produced by the decomposition of CH_3CHO may react too quickly based on its rate of hydrogen abstraction (see Table 2.I.2).

Appendix 2.I

TABLE 1. THE ABSTRACTION OF HYDROGEN ATOMS BY METHYL RADICALS FROM THE PHOTOLYSIS OF ACETONE

(Trotman-Dickenson and Steacie)

	Compound	$E_1 - \frac{1}{2}E_2$ (kcal)	$k_1/k_2^{\frac{1}{2}} \times 10^{11}$ * at 182° C	$P_1/P_2^{\frac{1}{2}} \times 10^4$	Number of "active" H-atoms	$k_1/k_2^{\frac{1}{2}} \times 10^{11}$ * at 182° C per "active" H-atom
	Ethane	10.4	3.8	6	6	0.6
	2,2-Dimethyl propane	10.0	6.3	6	12	0.5
	2,2,3,3-Tetramethyl butane	9.5	10.0	7	18	0.6
	n-Butane	8.3	21	3	4	4.5
○	n-Pentane	8.1	27	3	6	4.0
○	n-Hexane	8.1	33	3	8	3.8
	2-Methyl propane	7.6	42	3	1	37
○	2,3-Dimethyl butane	7.8	78	6	2	36
○	2,3,4-Trimethyl pentane	7.9	65	8	3	20
	Ethene	10.0	5.6	9	4	1.4
	Propene	7.7	23	3	3	8
	2-Butene	7.7	57	7	6	10
	2-Methyl propene	7.3	49	4	6	8
○	2,3-Dimethyl-2-butene	7.8	145	17	12	12
	1-Butene	7.6	66	8	2	33
○	1-Pentene	7.6	68	8	2	34
○	3-Methyl-1-butene	7.4	102	9	1	102
	Cyclopropane	10.3	2.1	4	6	0.4
	Cyclobutane	9.3	22	17	8	2.8
○	Cyclopentane	8.3	47	9	10	4.7
○	Cyclohexane	8.3	42	8	12	3.7
○	Benzene	9.2	1.9	1	6	0.3
○	Toluene	8.3	26	5	3	8.7
○	Methanol	8.2	11	2	3	3.7
○	Ethanol	8.7	38	11	2	19
○	Isopropanol	7.3	60	3	1	60
	Methylamine	8.4	36	8	3	12
	Dimethylamine	7.2	135	8	6	23
○	Trimethylamine	8.8	85	30	9	9.5
	Ammonia	10.0	2.4	6	3	0.8
○	Methyl ether	9.5	17	14	6	2.8
○	Isopropyl ether	7.3	72	3	2	36
	1-Butyne	9.1	66	35	2	33
	2-Butyne	8.6	64	20	6	11
○	Acetone	9.7	19	10	6	3.2

* Units of k are molecules, cm.^{3}, and seconds.

○ Compounds used as sensitizers.

TABLE 2. FURTHER RESULTS ON REACTIONS OF METHYL RADICALS

	Reactant	Radical Source	E, kcal.	k at 182° C $\times 10^{-6}$ mole^{-1} cm.^{3} sec.$^{-1}$	$P \times 10^4$	Reference
	2-Me propane	Acetone	7.6 ± 0.2	22	3	Trotman-Dickenson and Steacie [1955]
		$Hg(CH_3)_2$	7.3 ± 0.3	16	2	Rebbert and Steacie [2004]
		Azomethane	6.7 ± 0.3	10	~1	Jones and Steacie [1953]
○	Toluene	Acetone	8.3 ± 0.3	14	5	Trotman-Dickenson and Steacie [1955]
		$Hg(CH_3)_2$	7 ± 2	5	0.3	Smith and Taylor [1403, 1710]
		DTBP *	11 ± 2	—	—	Roberts and Szwarc [2021]
○	Methanol	Acetone	8.2 ± 0.2	6	2	Trotman-Dickenson and Steacie [1955]
		$Hg(CH_3)_2$	8.2 ± 0.5	5	2	Phibbs and Darwent [1950]
	Ethylene imine	DTBP *	4.8 ± 0.3	200	~10^{-4}	Brinton and Volman [599]
	Azomethane	Azomethane	7.6	~20	~3	Jones and Steacie [775]
○	Dimethyl ether	Acetone	9.5 ± 0.2	9	14	Trotman-Dickenson and Steacie [1955]
		$Hg(CH_3)_2$	8.4 ± 1.5	9	14	Phibbs and Darwent [1950]
		CH_3OCH_3	10 ± 2	12	19	Recalc. from Marcus, Darwent and Steacie [997]
	n-Butane	Acetone	8.3 ± 0.2	11	3	Trotman-Dickenson and Steacie [1955]
		$Hg(CH_3)_2$	8.2 ± 0.5	22	6	Gomer [664]
		$Hg(CH_3)_2$	9.5 ± 0.5	10	3	Gomer [664], Recalc.
		$Hg(CH_3)_2$	—	18	3	Smith and Taylor [1402, 1710]
		Azomethane	9.1 ± 0.3	—	~10	Jones and Steacie [1953]
	Cyclopropane	Acetone	10.3 ± 0.4	1.1	4	Trotman-Dickenson and Steacie [1955]
		$Hg(CH_3)_2$	10.2 ± 1.0	1.5	6	Phibbs and Darwent [1950]
	Ethylene oxide	$Hg(CH_3)_2$	9.0 ± 1.0	1.5	1.5	Gomer and Noyes [660]
		$Hg(CH_3)_2$	9.6 ± 2	2.8	5	Phibbs and Darwent [1950]
○	Acetaldehyde	DTBP *	8.0 ± 0.3	220	45	Brinton and Volman [599]
○	Acetone	Acetone	9.7 ± 0.1	10	10	Trotman-Dickenson and Steacie [1955]
		Acetone	9.6 ± 0.4	8	8	Saunders and Taylor. Recalc. [1860]
		Acetone	9.5 ± 0.2	11	10	Gomer and Kistiakowsky [668]
		DTBP *	9.5 ± 1.0	9	7	Jaquiss, Roberts and Szwarc [750]
○	Biacetyl	Biacetyl	7.1 ± 0.2	17		Biacet and Bell [1874]
○	Di-t-butyl peroxide	DTBP *	(15)	2		Brinton and Volman [599], Recalc.
	Mercury dimethyl	$Hg(CH_3)_2$	9.0 ± 0.5	10		Gomer and Noyes [660]
		$Hg(CH_3)_2$	11.0	3		Rebbert and Steacie [1950]
	Cadmium dimethyl	$Cd(CH_3)_2$	(14)	2		Anderson and Taylor [54]

* DTBP = Di-t-butyl peroxide.

Appendix 2.II.

Table i) Sensitivity Factors

All sensitivity factors are relative to oxygen (S.F. = 1.00)

Compound	S.F. (divide by)
HCHO	0.81
CH_3OH	1.42
3M1B1	1.70
224-TMP	0.93
O_2	1.00

Appendix 2.III

The Burrell KromoTog (TCD) was recalibrated with respect to the following gases and liquids: N_2, O_2, CH_4, CO, CO_2, H_2O and CH_3OH (Figures 2.III(i) and 2.III(ii)).

The results and corresponding sensitivity factors are included in Table 2.III. These factors were used to correct the peak areas, determined by the Hewlett Packard Minigrator M-2, to represent molar percentages.

Each component was calibrated at its respective elution temperature, i.e., N_2, O_2, CH_4, CO and CO_2 at 75°C and H_2O and CH_3OH at 175°C, using the dual column system of Molecular sieve 5A (column A) and Porapak T (column B). All samples were injected by syringe.

Table 2.III. Calibration of Burrell KromoTog (TCD) and determination of sensitivity factors.

Component	Slope of calibration curve Integ units/mole (-10^9)	Sensitivity Factor
N_2	1.625	1.11
O_2	1.485	1.0
CH_4	1.47	1.0
CO_2	1.95	1.33
CO	1.65	1.12
H_2O	1.45	1.0
CH_3OH	2.09	1.42

Figure 2.III.1
Liquids.

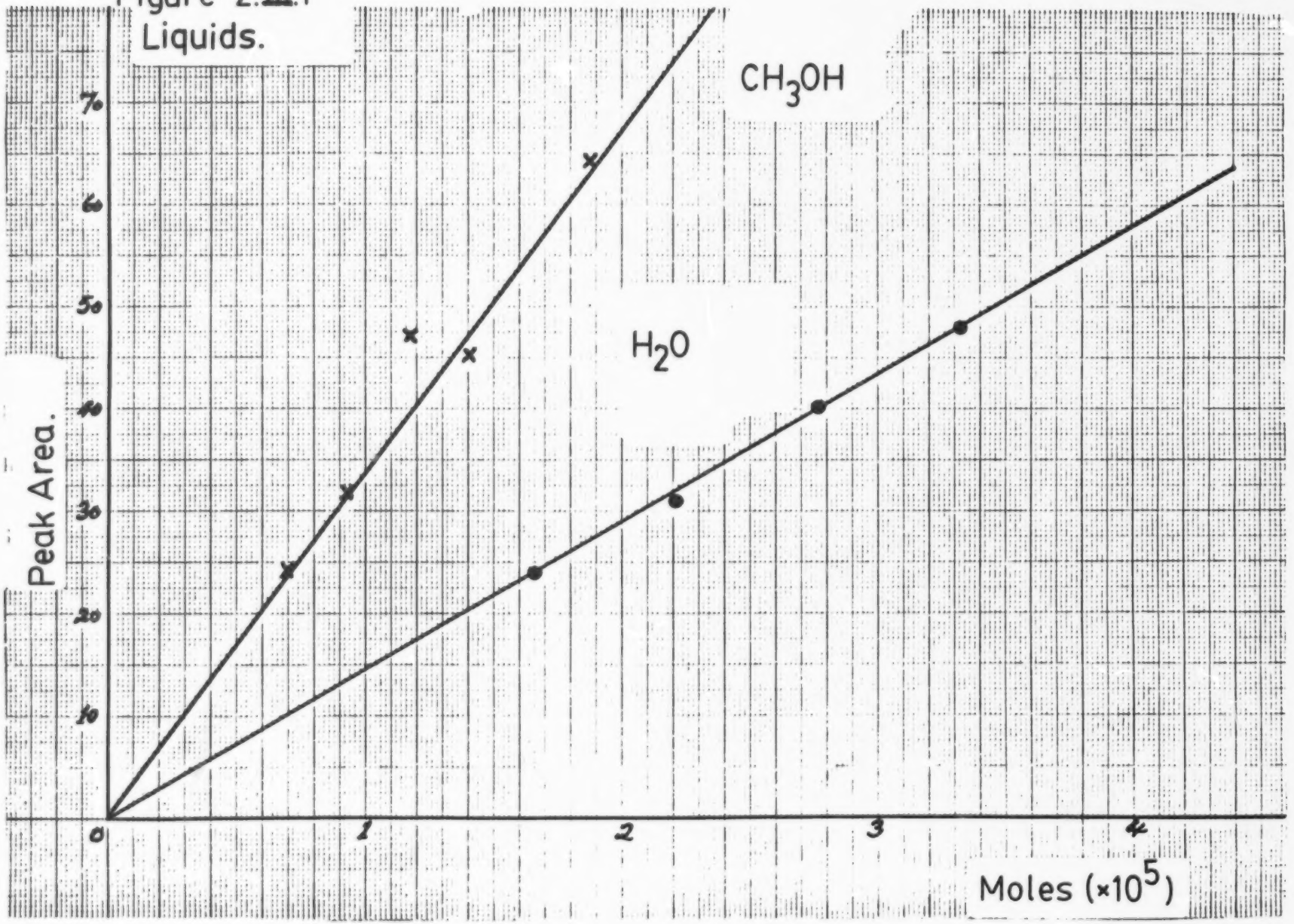
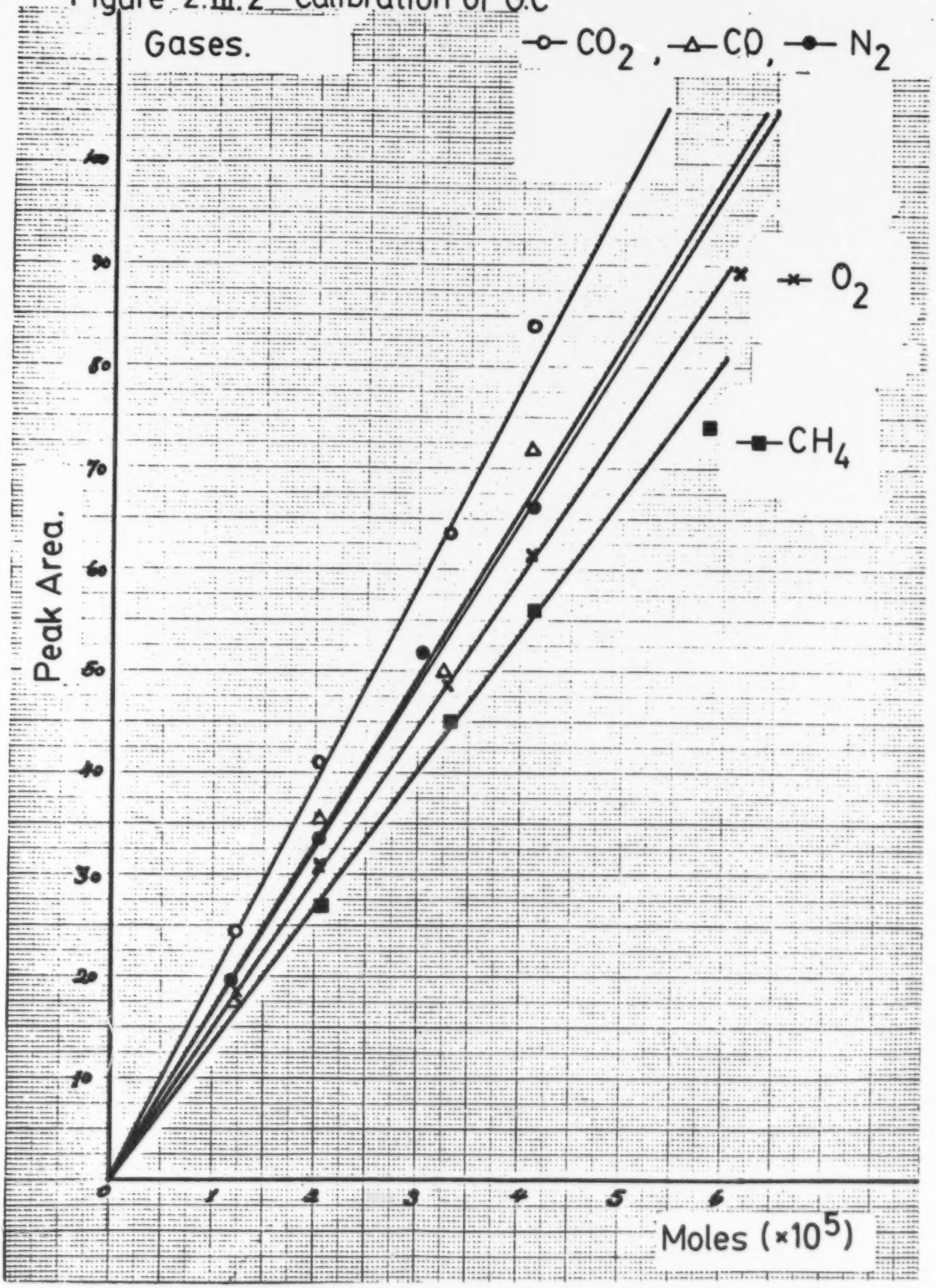


Figure 2.III.2 Calibration of G.C Gases.



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PART THREE

HG Sensitization (Task 4 Revised)

INTRODUCTION

This section describes the experimental procedure and results obtained to complete the revised Task 4, i.e. Hg photosensitization.

It is known that a molecule may be photodecomposed by transferring the energy from a metal vapour, excited by a suitable light source, to the molecule of interest.

In the case of methane sufficient energy is provided by the Hg 6^1S_0 to 6^3P_1 transition (253.7 nm) to dissociate one of the C-H bonds (see Table 3.1). This would produce a CH_3 radical, which is accepted as the first step in the methane oxidation scheme. As such the reaction will be photosensitized.

Susceptibility of the oxidation of methane to photosensitization should result in a reduction in the minimum temperature for complete reaction (MTCR)[1].

EXPERIMENTAL PROCEDURE

A Mercury-U.V. emission lamp (253.7 nm) was made from quartz (commercial grade) in the form of several coils (Figure 3.1) and equipped with electron emitting and collector plates.

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[1] see Bell and McDowell, Can. J. Chem. 39, 1419-1424 (1961) for a study at atmospheric conditions.

A bead of mercury was placed in the lamp before evacuation and the lamp was filled with Helium prior to being sealed. The lamp was connected to a high voltage transformer (15 Kv).

A reaction system incorporating a quartz reactor tube (Griffen Worden-Kontes Scientific Instruments) (operating pressure of 10 atm) wired with Nichrome heating wire (total resistance = 9), suitably spaced, and provided with two thermocouples, one inside the quartz reactor and one exterior to it, was constructed. A vernier valve (Ideal-Aerosmith) was connected at the inlet of the reactor to control the input gas flow of methane and oxygen (Figure 3.1).

An uncoated quartz Dewar was inserted between the quartz reactor and the Hg resonance lamp to offset the heat produced by the wire heating element and so keep the lamp cool.

The Quartz Reactor System (QRS) was calibrated with nitrogen for pressure, temperature and flow. The reaction volume was 65 mL.

The QRS replaced the previously used stainless steel reactor and associated furnaces, and therefore was subject to the same reactant gas controls and analytical system.

The reactant gas mixture of methane (containing ca 1.5% N_2) and oxygen was set to give an exit-flow rate of 40-50 mL/min (NTP) at 10 atm pressure and an oxygen concentration of 4.3%.

Prior to the reaction study a bead of mercury (ca 0.5 cm diam.) was introduced into the input end of the quartz reactor tube.

The effect of the Hg resonance radiation on the reaction was investigated by bringing the reactor temperature up to a point where reaction would proceed but was not complete, i.e. reactant oxygen not completely consumed (390°C). After reaching a steady state the Hg

resonance lamp was switched on and oxygen consumption, hence conversion of methane, and methanol yield, were monitored.

RESULTS AND DISCUSSION

Both the consumption of oxygen and the conversion of methane was increased at 390°C in the presence of the mercury resonance radiation (Tables 3.2 and 3.3). The reaction therefore underwent photosensitization. The improvement was slight, however, and the selectivity and yield of methanol fell due to the production of CO and CO_2 during photosensitization.

The temperature of 390°C was arrived at because it represented a point at which just over half of the available oxygen was consumed (fraction of O_2 consumed = 0.58 of critical $[O_2]$ = 4.29%).

Exposure of the oxidation reaction to the mercury resonance radiation increased the fraction of O_2 consumed to 0.8 from 0.6 in its absence.

The small effect of photosensitization may be linked to the low quenching cross section between mercury vapour and methane (Table 3.4).

The intensity of the U.V. light emitted from the mercury lamp was equivalent to 7.48×10^{-17} quanta/mL/s and was considered to be a reasonable energy output (see Appendix 3.I).

CONCLUSION

The oxidation of methane was photosensitized by mercury resonance radiation to the extent that 40% increase in the amount of oxygen reacted compared to the non-photosensitized reaction (Tables 3.2 and 3.3). At 390°C, upon absorbing 7.5×10^{17} quanta mL^{-1} s^{-1}, the oxidation reaction consumed 80% of the available oxygen effecting a methane conversion of 2.52%. In the absence of the resonance u.v. radiation only 57% of the available oxygen was consumed corresponding to a methane conversion of 2%.

Sensitization of the oxidation reaction by external means would certainly seem to hold some potential with regard to reducing the reaction temperature.

Table 3.1. Resonance Levels of Metal Vapors[2].

Metal	Resonance Level	Wavelength of Line, Å
Na	3^2P	5890/96
Hg	6^1P_1	1849
	6^3P_1	2537
Cd	5^1P_1	2288
	5^3P_1	3261
Zn	4^1P_1	2139
	4^3P_1	3076

[2]Atomic and Free Radical Reaction, E.W.R. Steacie, Vol. I, 2nd Ed., Publ. Reinhold, N.Y. (1954).

Table 3.2. Oxidation of CH_4 with O_2 - No Photosensitization.

Pressure = 8.30 atm Reactor Temp. = 389°C (inner)

$\%N_2$ = 1.81 ± 1.23 = 326°C (outer)

CH_4/N_2(reactant) = 51.18 RFR = 95s(reac. vol)$^{-1}$ NTP

O_2/N_2(reactant) = 2.37

S.T.(reactor = 351s(reac. vol)$^{-1}$ $\%[O_2]$ = 4.29 ± 1.77

	O_2	N_2	CO_2	CH_4	CO	H_2O	CH_3OH
% Area	1.82	1.82	N.D.	89.22	N.D.	5.27	1.86
% Selectivity							100
C/N_2				48.90			1.02
O_2/N_2	1.00					1.44	0.50

% Conversion = 2.04 % C. bal. = 97.54

% Yield = 2.04 % O_2 bal. = 124.23

Frac. O_2 consumed = 0.575 (= 2.48% O_2 absolute)

For examples of calculations of conversion, yield and selectivity, see Table 3.3.

Table 3.3. Oxidation of CH_4 with O_2 - Photosensitization.

Pressure = 8.30 atm

Reactant Input data as Table 3.2

Temp. of Hg bead = 58°C

S.T.(reactor) = 374s(reac. vol)$^{-1}$

Reactor Temp. = 391°C (inner)

= 331°C (outer)

RFR = 100s(reac. vol)$^{-1}$ NTP

%[O_2] = 4.29 ± 1.77

	O_2	N_2	CO_2	CH_4	CO	H_2O	CH_3OH
mol % Area	0.85	1.81	0.38	90.31	0.46	4.69	1.50
% Selectivity			16.39		19.52		64.09
C/N_2			0.225	49.81	0.268		0.88
O_2/N_2	0.50		0.225		0.134	1.38	0.44

% Conversion = 2.68

% Yield = 1.72

% C. bal. = 100.00

% O_2 bal. = 113.04

Frac. O_2 consumed = 0.79 (= 3.39% O_2 absolute)

$$\% \ CH_4 \text{ conversion} = \left[\frac{\Sigma(CH_4/N_2)_{reactant} - (CH_4/N_2)_{products}}{(CH_4/N_2)_{reactant}}\right] \times 100$$

$$= [(51.18 - 49.81) / 51.18] \times 100$$

$$= 2.68$$

$$\% \text{ methanol selectivity} = [(CH_3OH/N_2) \ / \ \Sigma(C/N_2 \text{ oxidised species})] \times 100$$

$$= 64.09\%$$

$$\% \text{ methanol yield} = (\% \text{ selectivity} \times \% \text{ conversion}) / 100$$

$$= 1.72$$

as per definitions in Part One

Table 3.4. Quenching cross sections ($\sigma_Q 2$) for Hg atoms in the $^3P_1$ state[2] for species of interest[3].

Compound	$\sigma_Q 2$ (A^2)
H_2	8.6
N_2	0.274
H_2O	1.43
CO	5.82
CO_2	3.54
CH_4	0.084
O_2	19.9
CH_3OH	11.0

[3]A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge University Press 1934, Reprinted 1961.

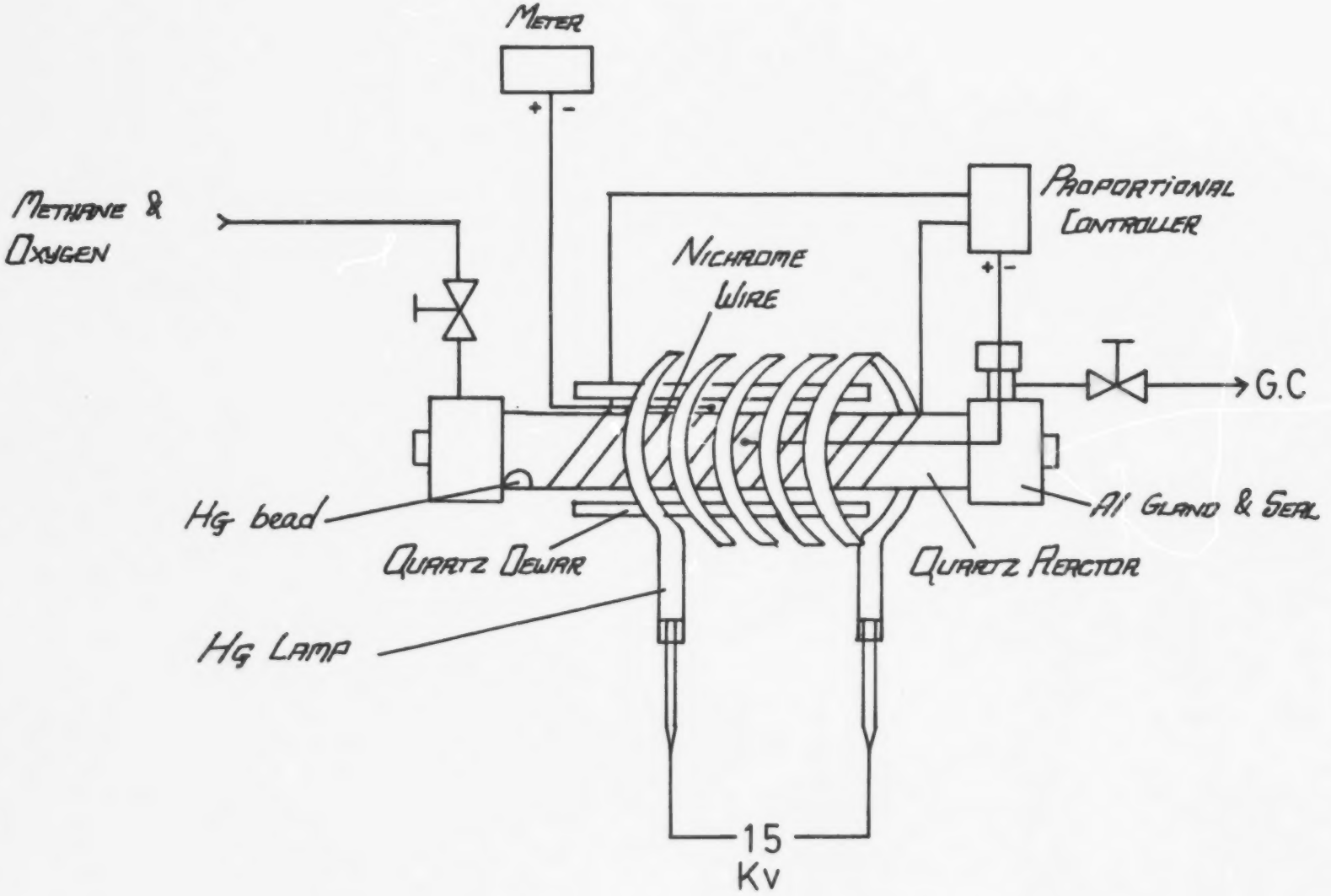

Figure 3.1 QUARTZ REACTOR SYSTEM.

Appendix 3.I. Determination of Hg lamp intensity[4].

Incident light intensity: $\Phi_{253.7}$

$$\Phi_{253.7} = \frac{1}{\Phi_{253.7}} \times \frac{1}{\varepsilon} \times \frac{\Delta A}{\Delta t} \times \frac{25}{3}$$

$$\varepsilon = 1.12 \times 10^{4} \text{ L mole}^{-1} \text{ cm}^{-1}$$

$\Phi_{253.7}$ = 1.25; quantum yield for 253.7 nm radiation

$$\frac{\Delta A}{\Delta t} = 9.565 \times 10^{-3} \text{ s}^{-1}$$

$\Delta A/\Delta t$ determined from Lambert-Beer plot of absorbance by a solution of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ (6×10^{-2} M) versus Hg lamp irradiation time. The ferrioxalate photodecomposes to ferrous oxalate in acid solution

$$2Fe(C_2O_4)_3^{3-} + h\nu \longrightarrow 2FeC_2O_4 + 3C_2O_4^{2-} + 2CO_2$$

The light source intensity is directly related to the $[Fe^{2+}]$

$$\Phi_{253.7} = \frac{1}{1.25} \times \frac{1}{1.12} \times 10^{-4} \times 9.565 \times 10^{-3} \times \frac{25}{3}$$

$$= 6.693 \times 10^{-4} \text{ einstein L}^{-1} \text{ s}^{-1}$$

$$\text{Total energy of lamp} = \frac{\text{vol of } Fe(C_2O_4)_3}{\text{vol assayed}} \times \Phi_{253.7}$$

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[4]Huminicki, P. G., M.Sc. Thesis, University of Manitoba (1979).

$$= \frac{39}{3} \times 9.565 \times 10^{-5}$$

$$= 1.243 \times 10^{-3} \text{ einstein } L^{-1} s^{-1}$$

$$1 \text{ einstein} = 6.023 \times 10^{23} \text{ quanta}$$

$$\text{Light Intensity Energy of Lamp} = 7.48 \times 10^{17} \text{ quanta } mL^{-1} s^{-1}$$

PART FOUR.

Kinetic Model Study [Task 5(A)]

1. Determination of Rate Parameters for the Methane Partial Oxidation Reaction

In order to obtain the Arrhenius parameters for the partial oxidation reaction namely, $CH_4 + O_2 \longrightarrow$ Products, about forty experiments were performed during which the oxygen concentration in the feed, reaction temperature and residence time were varied. In all the experiments the reactor pressure was maintained between 25-30 atm. For each of the experiments detailed product distribution was obtained. Furthermore, conversions (based on CH_4) were calculated.

Table 4.1 summarises the results obtained in a set of experiments conducted at an oxygen concentration of 10.1 mol % in the feed gas. The results obtained at 5.5 mol % oxygen concentration in the feed gas are given in Table 4.2.

Using the conversion values presented in Tables 4.1 and 4.2 rate constants were obtained at each of the reaction temperature by the following procedure.

$$\underset{(A)}{CH_4} + \underset{(B)}{O_2} \longrightarrow \text{Products} \qquad (1)$$

The reactor was assumed to be operating in a true plug-flow mode and to begin with the reaction was assumed to be following first order kinetics.

For a 1st order irreversible reaction with constant density, a simplified form of rate expression is,

$$k\tau = -\ln (1-X_A) \qquad (1)$$

where k = rate constant, sec^{-1}

τ = residence time (at reactor inlet conditions)

X_A = fractional molar conversion of CH_4

on rearranging eq. 1 we obtain,

$$\log (1-X_A) = \frac{-k}{2.303} \cdot \tau \qquad (2)$$

Hence, a plot of $\log (1-X_A)$ vs τ for a given reaction temperature should result in a straight line, provided the above assumptions were true. On plotting $\log (1-X_A)$ vs τ at various temperatures for a fixed O_2 concentration in the feed gas, a family of straight lines were obtained. The slopes of these lines give the values of rate constants. A step by step calculation procedure is given in the Appendix 4.I. In Tables 4.3 and 4.4 the rate constants at various reaction temperatures are presented for the fixed O_2 concentrations of 10.1 mol % and 5.5 mol % respectively. Using the above data, Arrhenius plots ($k = A \cdot e^{-Ea/RT}$) were constructed and are shown in Figures 4.1 and 4.2 for the O_2 concentrations of 10.1 and 5.5 mol % respectively. The frequency factor and the activation energy for each case are given below.

O_2 Concentration in the Feed Gas, mol%	Activation Energy Ea, kcal/mol	Frequency Factor, A sec^{-1}
5.5	35.1	1.78×10^8
10.1	14.4	8.06×10^3

Examination of the above data shows that an increase in oxygen concentration in the feed gas lowers the activation energy. However, even at 5.5 mol% O_2 concentration level, the activation energy was 35.1 kcal/mole, which is lower than the activation energy required for the initiation step namely the hydrogen abstraction reaction.

$$CH_4 + O_2 \longrightarrow CH_3 + HO_2 \qquad (Ea = 55.0 \text{ kcal/mole})$$

Arrhenius parameters were also obtained using the O_2 conversion values. In Tables 4.5 and 4.6 the rate constants (based on O_2 conversion) are presented for the two different feed gas compostiions. The frequency factor and activation energy for each case are given below. Furthermore, the Arrhenius plots are shown in Figures 4.3 and 4.4 respectively for the two levels of O_2 concentration in the feed gas.

O_2 Concentration in the Feed Gas, mol %	Activation Energy Ea, kcal/mol	Frequency Factor, A sec^{-1}
5.5	38.5	7.832×10^{10}
10.1	45.1	1.122×10^{13}

2. Variation in Formaldehyde Formation with Respect to Reaction Temperature

Formaldehyde in the product stream was estimated by using the modified pararosaniline method. Essentially the procedure involved is as follows: The product stream at a known flow rate and for a given time period was bubbled through 25 mL of distilled water placed in a bubbler. From this stock solution, 0.1 mL was further diluted to 25 mL solution including 2 mL of stock pararosaniline and 2 mL of stock sodium sulfite solution. The final solution was kept in a water bath at 25°C for 1 h so as to develop the color. The absorbance at 570 nm was determined using a spectrophotometer. From the calibration curve, the amount of formaldehyde was estimated.

The yield of formaldehyde was determined as a function of reaction temperature (run #102 & 103) at an O_2 concentration level of 10.1 mol % in the feed gas. The data is presented in Table 4.7.

Interestingly, as can be seen from the data, the formaldehyde content in the product stream increased with increase in reaction temperature to a maximum value and later decreased with further rise in reaction temperature. At both the feed flow rates (90 and 150 mL/min at NTP), the maximum amount of formaldehyde was obtained at a reaction temperature of about 391°C. At higher reaction temperatures, it is possible that formaldehyde may decompose to CO and H_2, in effect lowering its yield.

CONCLUSIONS

The kinetic expression assumes lst order kinetics with respect to CH_4 and then O_2. It is obvious that this is incorrect in the first case since $\frac{-d[CH_4]}{dt} = k[CH_4][O_2]$ is valid if $[O_2]$ is constant. This is not correct and so the values obtained for the kinetic parameters are in error.

In the second case the value of $[CH_4]$ is almost constant and the relation

$$\frac{-d[O_2]}{dt} = k[CH_4][O_2] = k_2[O_2]$$

is valid since the conversion is low, i.e. $[CH_4]$ changes only slightly (5-15 mol %) down the reactor tube.

This explains the more consistant value for the activation energy when considering the oxygen reactivity.

It must be pointed out that the exact order of the reaction with respect to O_2 may not be one. The results, however, are sufficiently consistent to support the assumptions made.

The mechanism of the reaction is a complex free radical chain mechanism and it is not possible to associate the activation energy to particular slow steps.

APPENDIX 4.I

The detailed procedure for obtaining the rate constants and the Arrhenius parameters for each of the set of reaction conditions is described in this Appendix. Data from Table 4.1 is made use of in illustrating the procedure.

1. Using data from Table 4.1. CH_4 conversion is plotted against the reaction temperature for each of the feed gas flow rates, as shown in Figure 4.I.1.
2. Figure 4.I.2 shows a plot of CH_4 conversion vs total feed gas flow rate (measured at NTP) for different reaction temperatures.
3. Later, CH_4 fractional conversion (X_A) is plotted against residence time (, calculated at reactor inlet conditions) and such a plot for different reaction temperatures is shown in Figure 4.I.3.
4. In Figure 4.I.4, log ($1-X_A$) is plotted against residence time , for different reaction temperatures. The slope of each of these lines gives the value of rate constant (k/2.303) at that reaction temperature.
5. The ln k vs 1/T (Arrhenius) plot is shown in Figure 4.1. From the slope and intercept, values of activation energy, E_a and frequency factor, A, are obtained.

The above procedure is repeated for the second set of experimental data (Table 4.2).

Table 4.1. Summary of process conditions and the conversions obtained during CH_4 oxidation.

Pressure = 26-30 atm

O_2 Concentration = 10.1 mol%

Volume of reactor = 13 cm^3

Run #	Feed flow rate (at NTP) mL/min	Temperature °C	Conversion, mole% Based on CH_4 fed	Based on O_2 fed
100	30	347	5.4	24.2
		354	8.1	55.9
		365	15.3	100.0
		380	15.3	100.0
		395	15.3	100.0
		419	15.3	100.0
101	60	356	2.4	8.9
		361	12.9	21.3
		374	17.2	100.0
		392	17.2	100.0
		417	17.2	100.0
102	90	361	2.4	1.1
		371	7.5	50.0
		382	11.4	80.6
		392	16.7	100.0

103	120	359	0.8	1.1
		369	5.5	18.8
		381	6.8	43.8
		398	12.7	100.0
104	150	362	0.1	0.5
		372	1.2	10.3
		391	9.6	82.3
		402	12.0	100.0

Table 4.2. Summary of Process Conditions and Conversion Obtained during CH_4 Oxidation.

Pressure = 26-28 atm

O_2 Concentration = 5.5 mol%

Reactor volume = 13 cm^3

Run #	Feed Flow Rate (at NTP) mL/min	Temperature	Conversion, mol %	
			Based on CH_4 fed	Based on O_2 fed
110	90	343	0.1	6.1
		353	0.5	12.5
		363	2.4	32.5
		374	6.3	81.0
		387	10.1	100.0
111	120	352	0.4	2.5
		364	1.5	22.0
		374	3.6	46.8
		384	6.6	98.3
		394	10.0	100.0
112	150	352	0.2	3.2
		362	0.8	6.4
		378	4.0	51.1
		394	8.2	100.0
		400	10.1	100.0

Table 4.3. Summary of reaction rates, rate constants and Arrheniums parameters for the data presented in Table 4.1.

T°C	r, $X10^{-4}$ (mol/sec/reactor volume)	k, $X10^{-4}$ sec^{-1}
370	5.666	5.743
375	6.410	6.681
380	7.126	7.454
385	7.857	7.880
390	8.333	8.507

Activation energy, Ea = 14.4 kcal/mole

Frequency factor, A = 8.01×10^{3} sec^{-1}

Table 4.4. Rate constants and Arrhenius parameters for the data presented in Table 4.2.

T°C	k, x 10^{-4} Sec^{-1}
370	2.3306
375	2.9524
380	3.9266
385	4.5346
390	4.7442

Activation energy, Ea = 35.1 kcal/mole

Frequency factor, A = 1.78×10^{8} sec^{-1}

Table 4.5. Rate constants and the Arrhenius parameters for the data presented in Table 4.1. (Using O_2 Conversions Values) 26-30 Atm, 10% O_2.

T°C	k, x 10^{-4} sec^{-1}
370	59.051
375	76.765
380	86.030

Activation energy, E_a = 38.5 kcal/mole

Frequency factor, A = 7.832 x 10^{10} sec^{-1}

Table 4.6. Rate constants and Arrhenius parameters for the data presented in Table 4.2. (Using O_2 conversion values) 26-28 Atm, 5.5% O_2.

T°C	k, x 10^{-4} sec^{-1}
360	25.701
365	37.423
370	51.817
375	57.575
380	83.163

Activation energy, E_a = 45.1 kcal/mole

Frequency factor, A = 1.122 x 10^{13} sec^{-1}

Table 4.7. Variation in the yield formaldehyde in the product stream with respect to reaction temperature.

Run #	Feed flow Rate mL/min	Reaction Temperature °C	Concentration of CH_2O in Exit % W/V
102	90	358	3.36×10^{-2}
		369	4.02×10^{-2}
		391	3.69×10^{-2}
		417	2.20×10^{-2}
103	150	360	4.31×10^{-3}
		371	2.32×10^{-3}
		379	1.67×10^{-3}
		392	3.33×10^{-2}
		415	2.27×10^{-2}

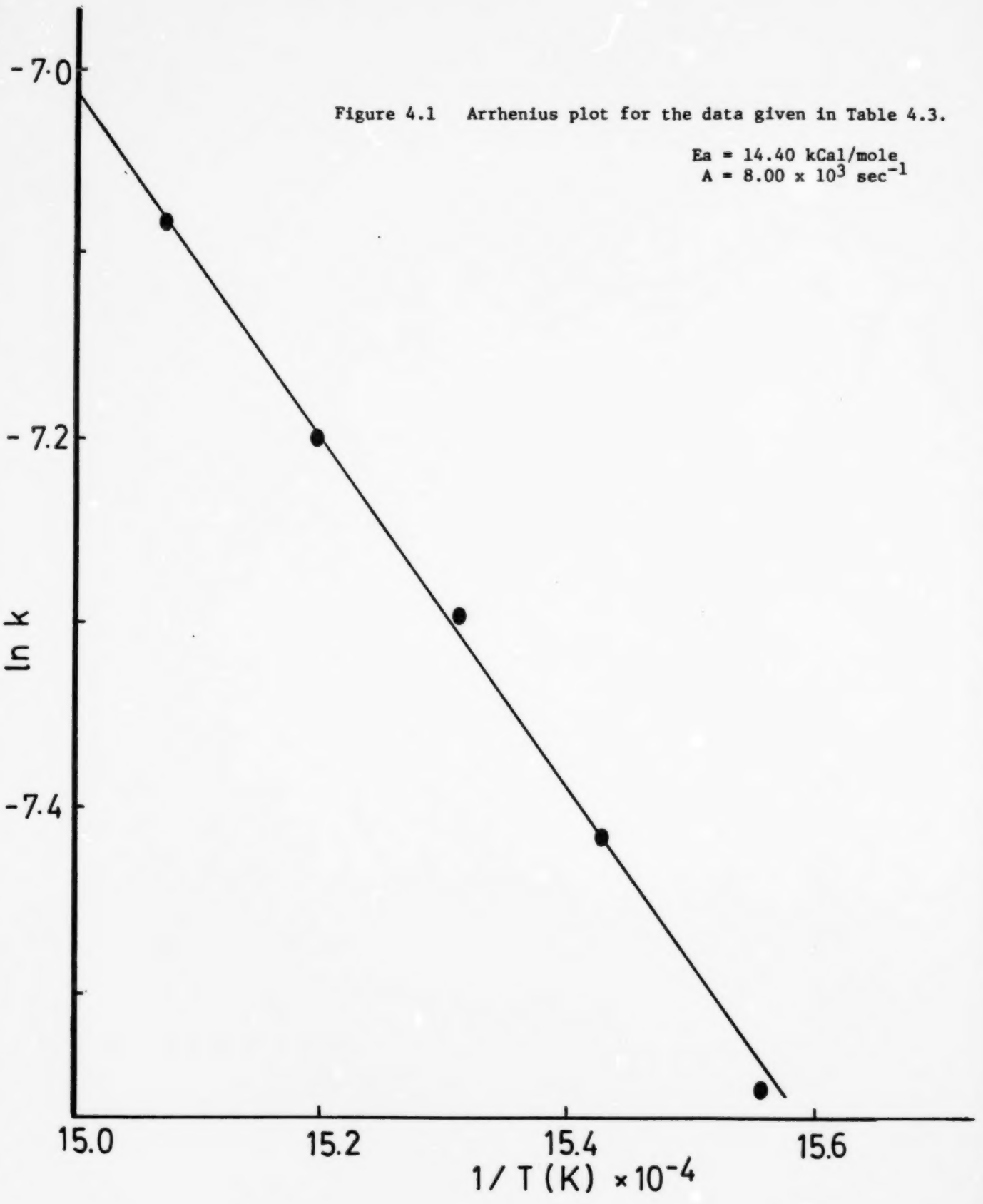


Figure 4.1 Arrhenius plot for the data given in Table 4.3.

Ea = 14.40 kCal/mole
A = 8.00 x 10^3 sec^{-1}

Figure 4.2 Arrhenius plot for the data given in Table 4.4.

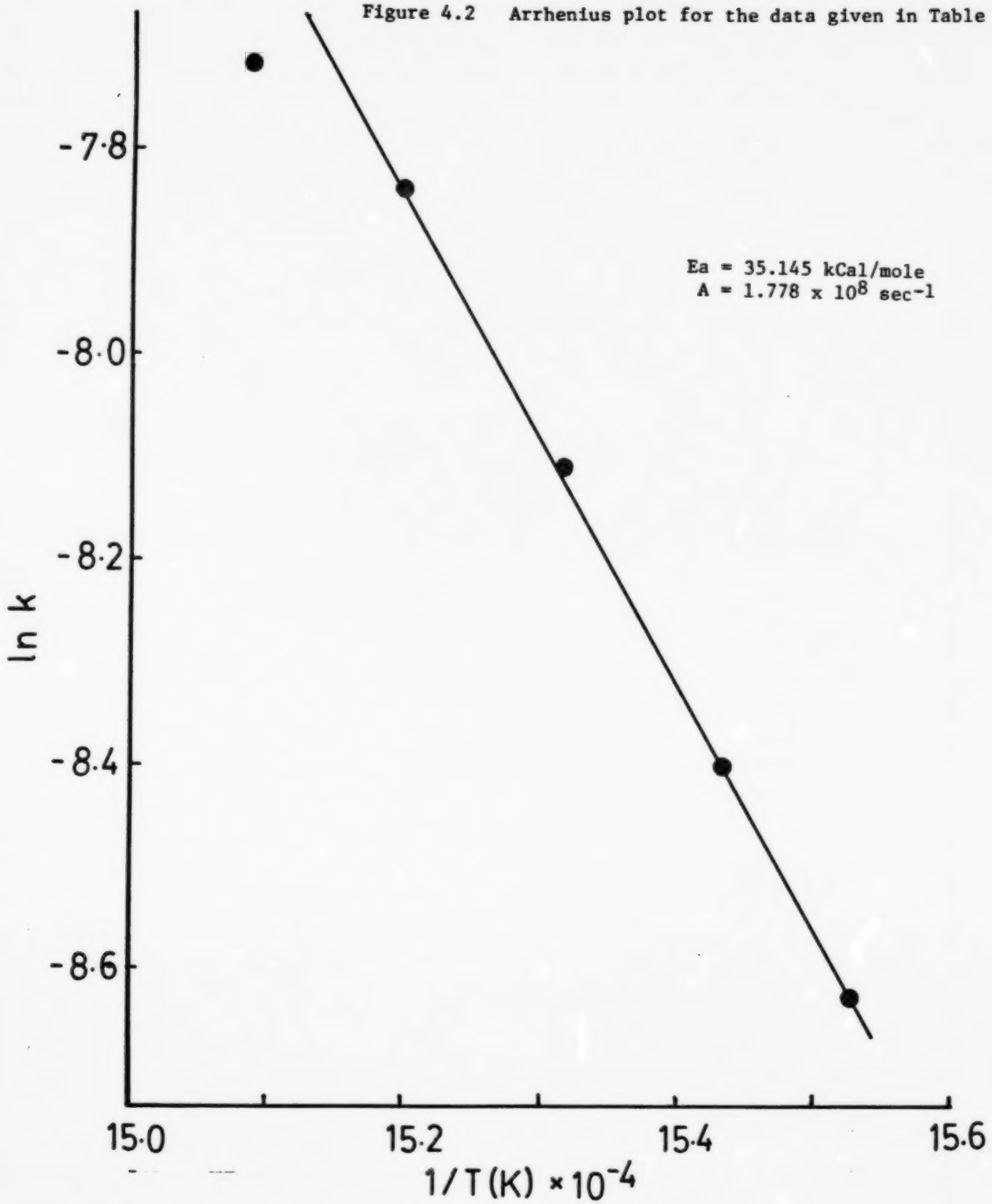


Figure 4.3 Arrhenius plot for the data given in Table 4.5.

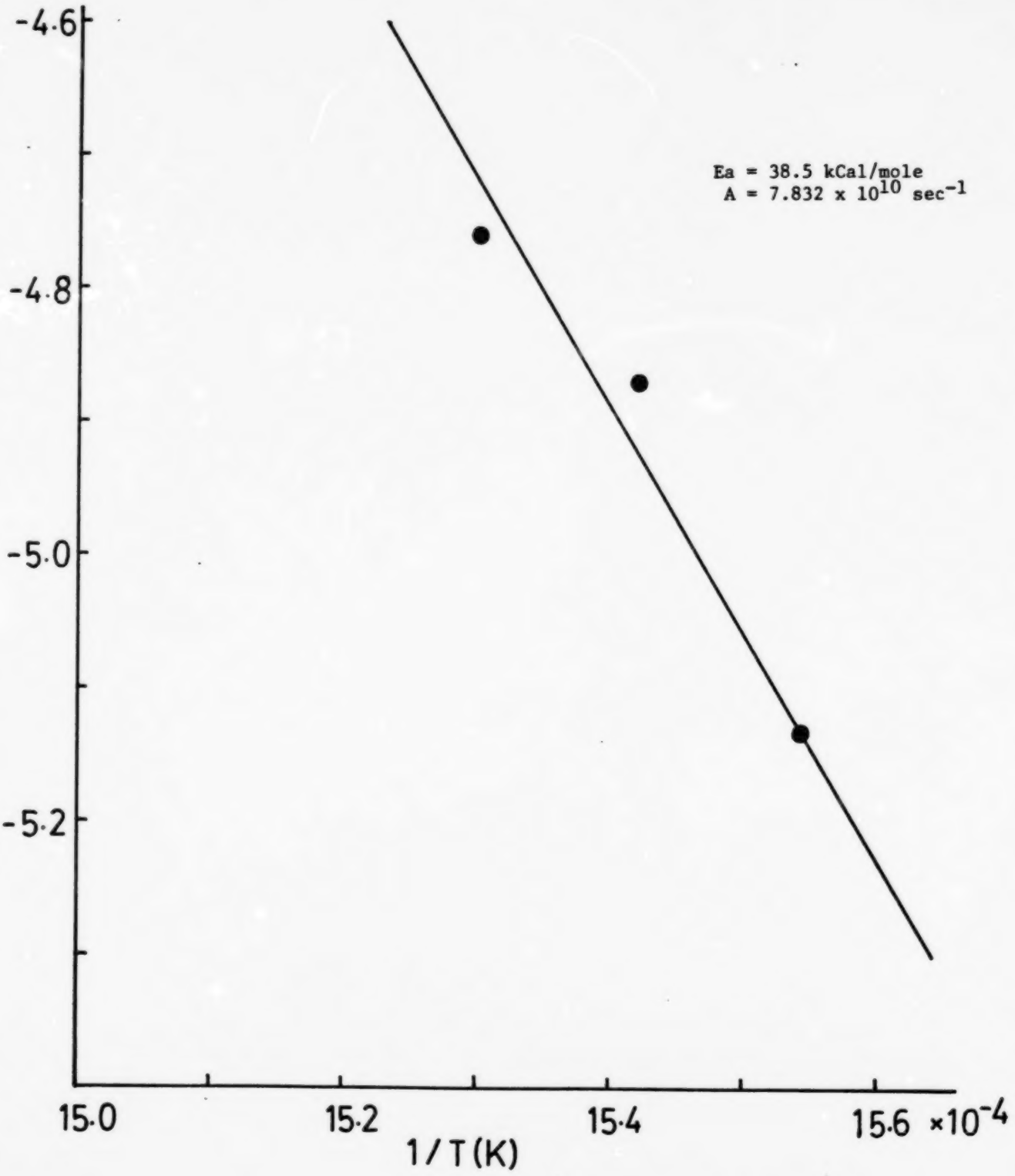
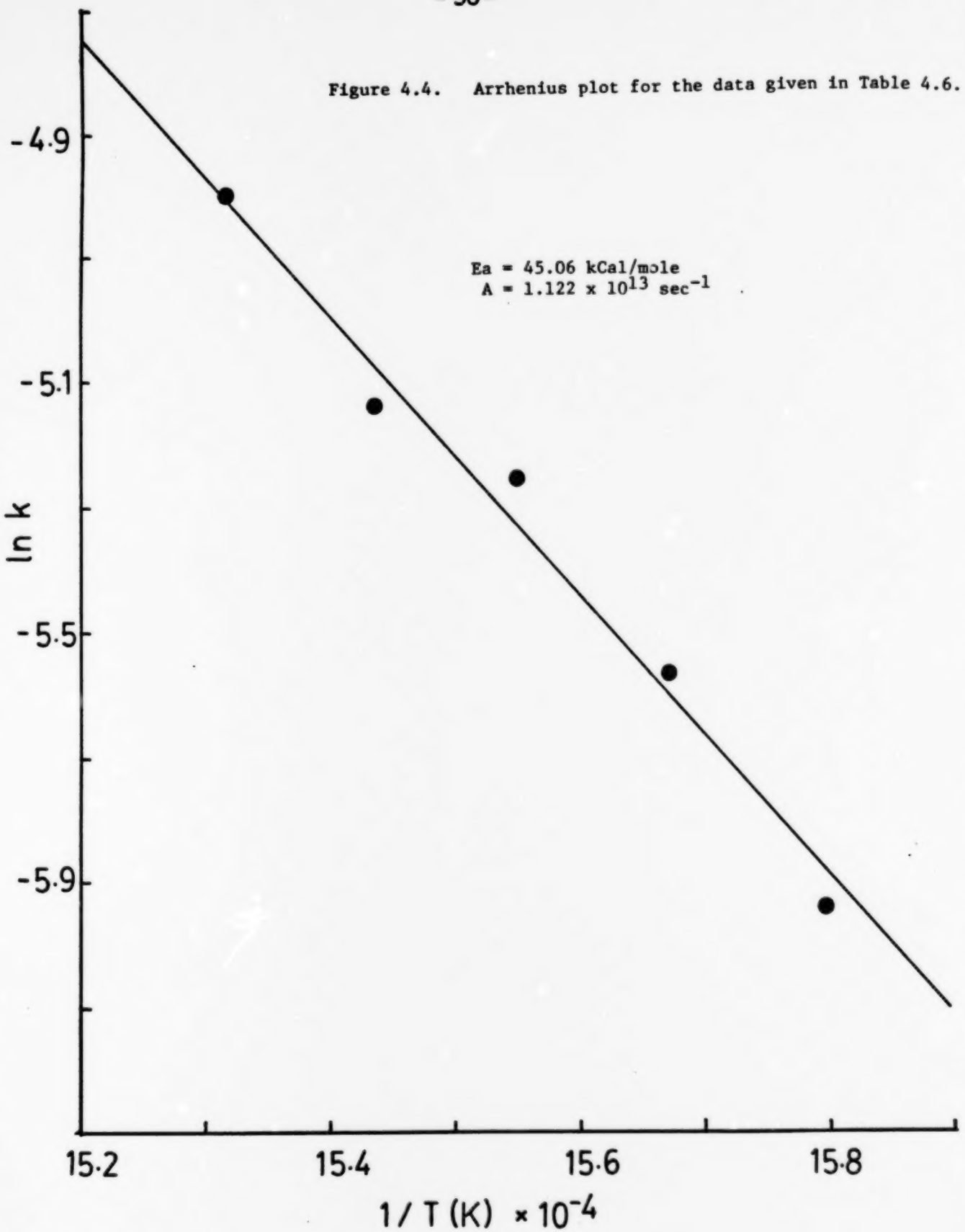


Figure 4.4. Arrhenius plot for the data given in Table 4.6.



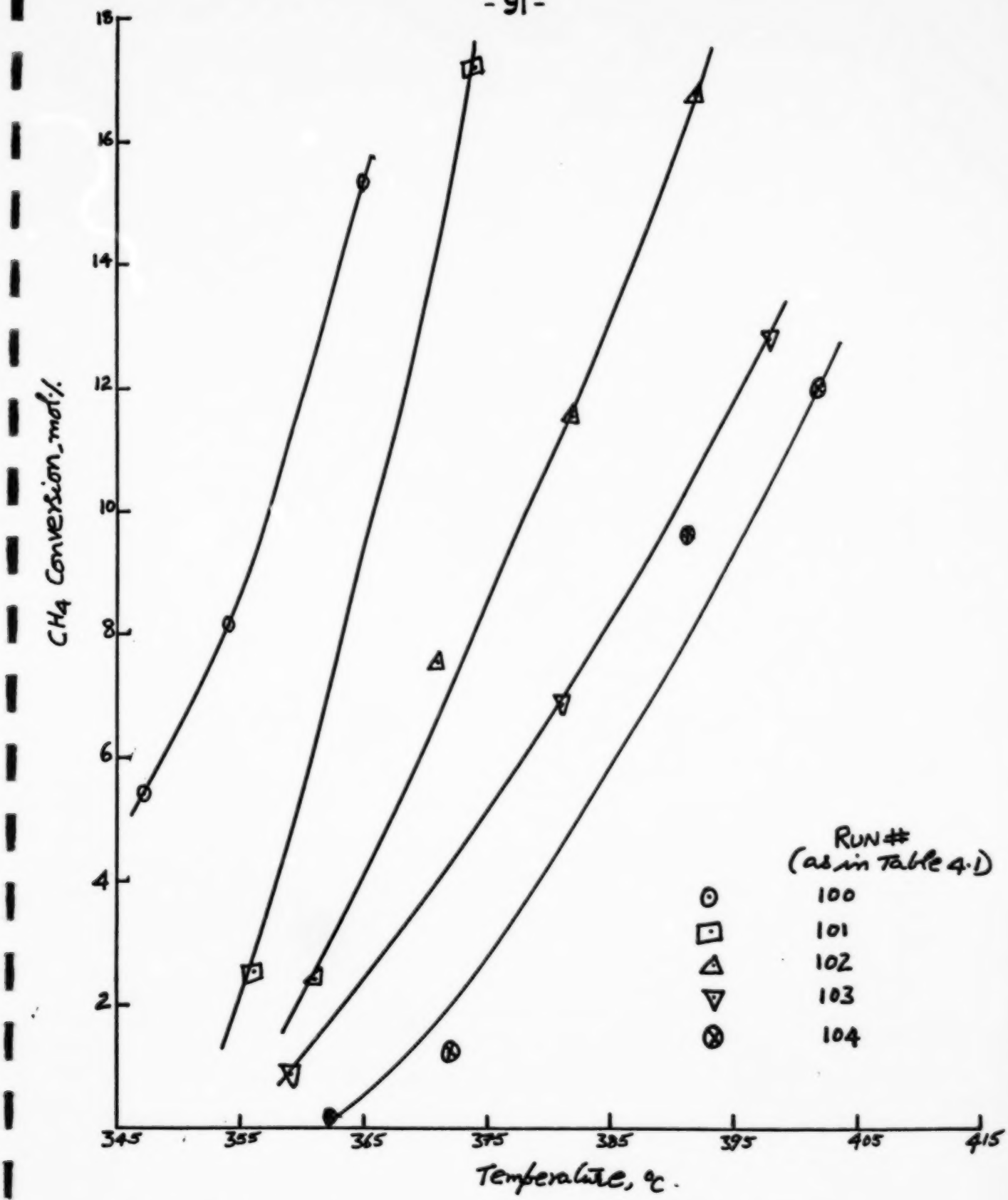


Fig. 4.11. Plot of CH_4 conversion as a function of reaction temperature for different feed gas flow rates.

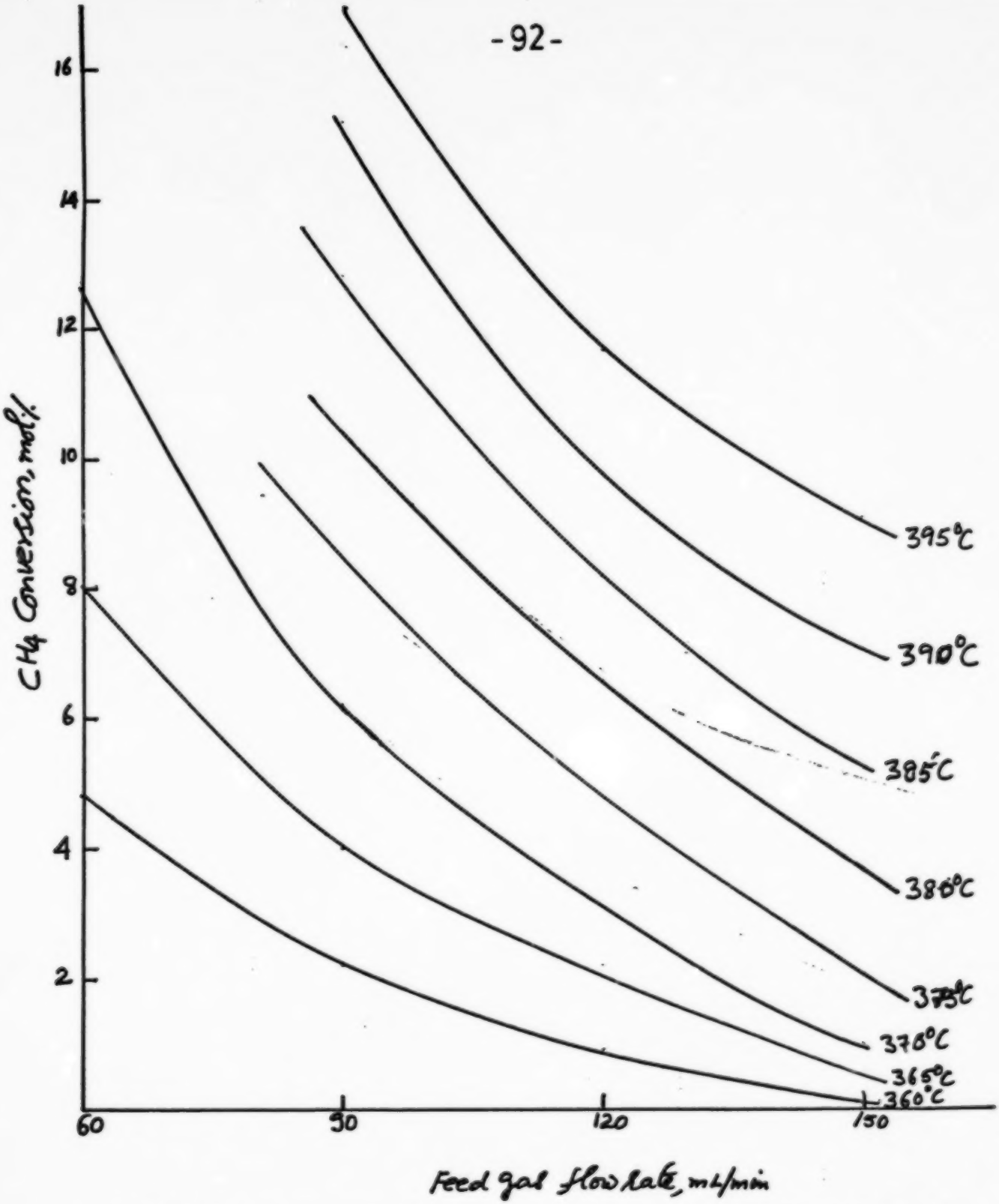


Fig. 4.12. Plot of CH_4 conversion as a function of feed gas flow rate at different reaction temperatures.

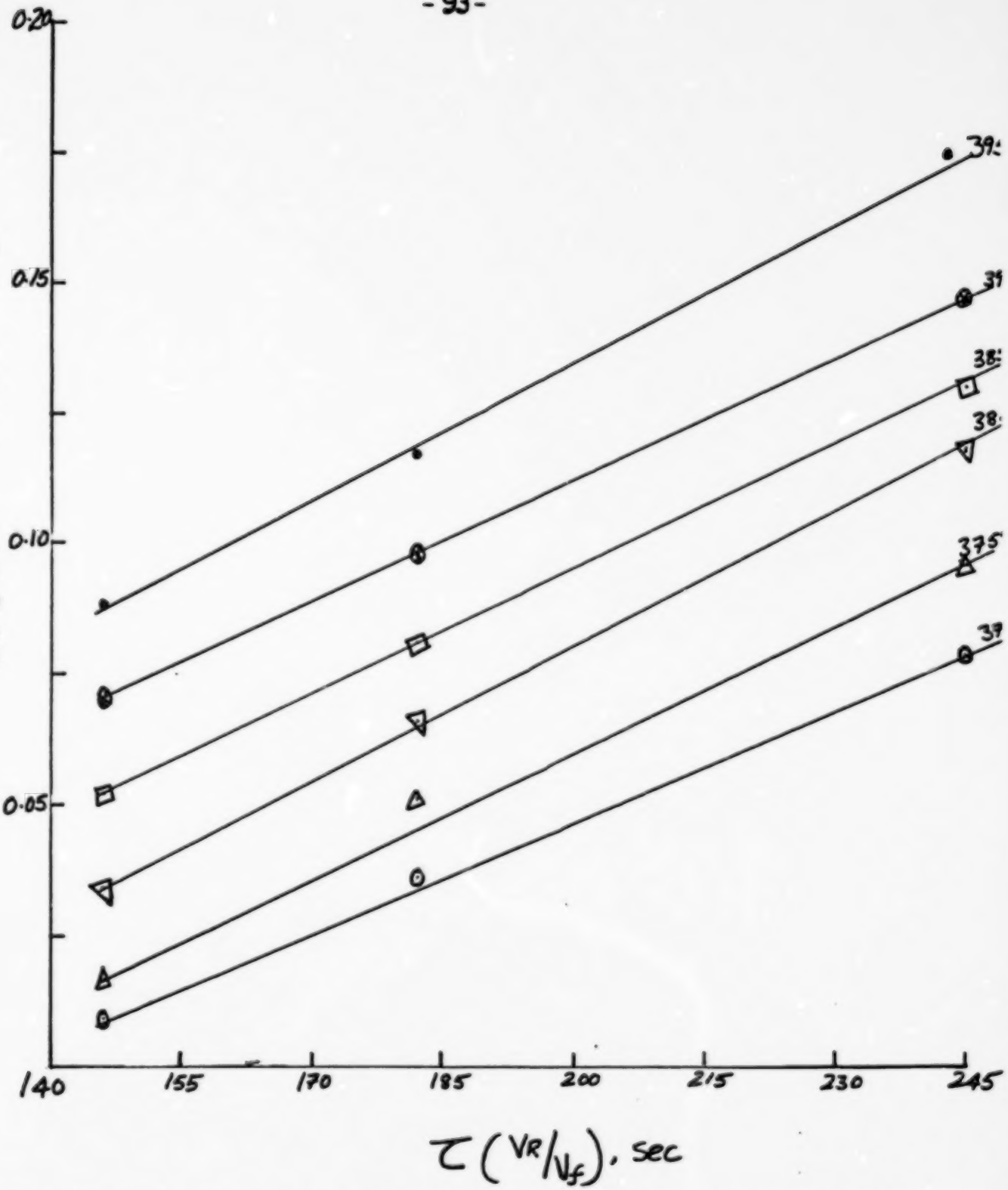


Fig. 4.13. Plot of CH_4 fractional conversion(X_A) as a function of contact time (τ) at different reaction temperatures.

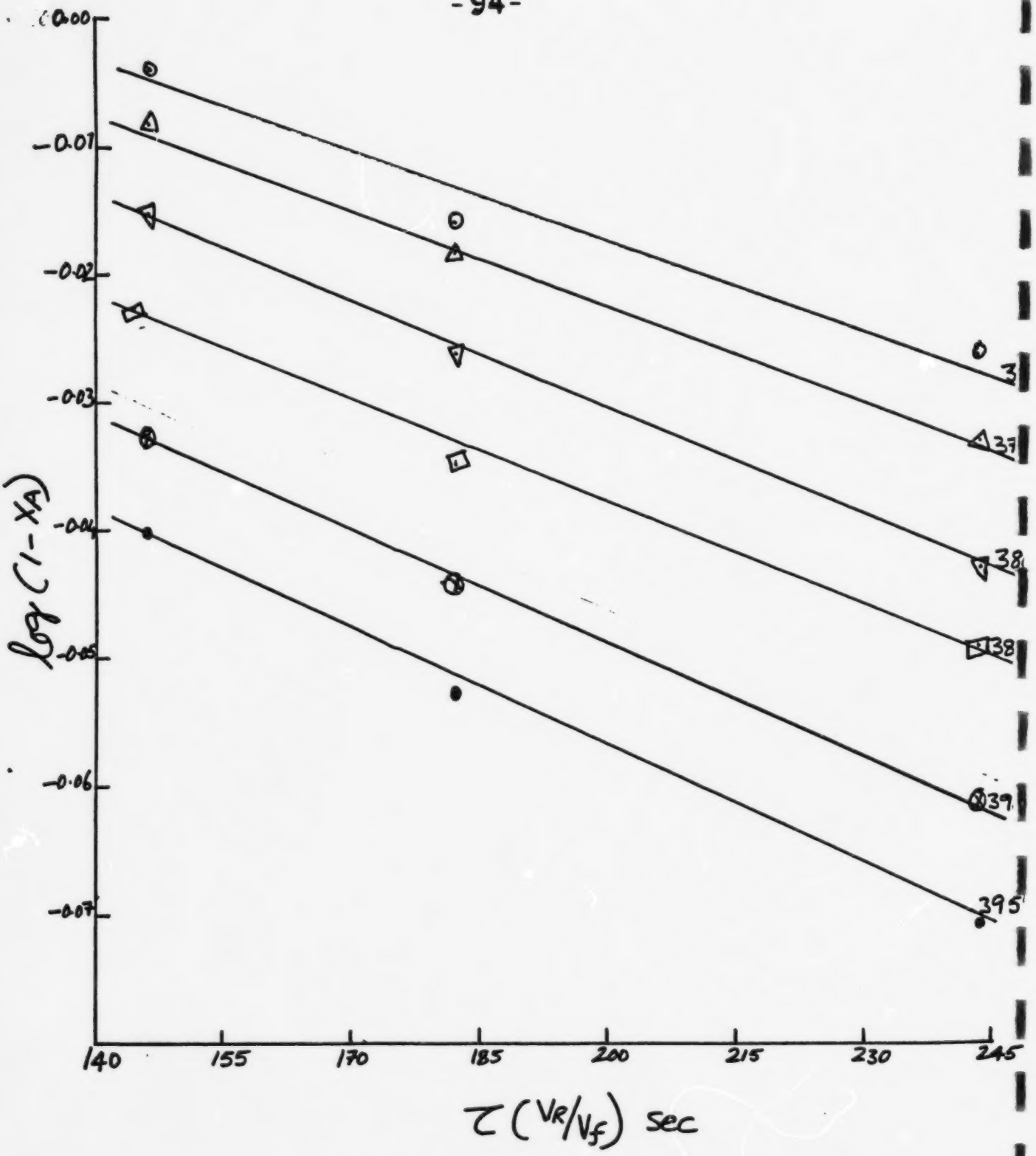


Fig. 4.14. Plot of log $(1-X_A)$ as a function of contact time (τ) at different reaction temperatures.

PART FIVE

Recycling Experiments [Task 5(B)]

INTRODUCTION

This section details the work carried out to complete Task 5(B) and the ensuing results.

A series of Recirculation experiments (IV-VIII) were designed to determined the effect, if any, of carbon monoxide and carbon dioxide at various concentration levels on the rate of methanol formation from the oxidation of methane. Both CO and CO_2 would be recycled into the main feed system and subsequently into the reactor and not removed as in previous recirculation experiments.

RECYCLE SYSTEM

The Recycle system was constructed as shown in (Figure 5.1). Two aluminum condensers, in series, were fitted to the system for the removal of the condensible liquids.

The apparatus was pressure checked with nitrogen to 48 atm and the Safety Relief Valves set as follows: SRV1 and SRV2 to relieve at 40 atm and SRV3 to 54 atm to allow for overpressurization of the Recycle Gas Storage Cylinder.

EXPERIMENTAL PROCEDURE - Recirculation IV

The whole apparatus was evacuated and the Recycle system

pressurized to 4.4 atm with CO_2 17 atm and CO 2.7 atm and isolated (valve A to valve C) from the rest of the system. This procedure reduced considerably the time to pressurize the Recycle system with Reactor Gas alone. These amounts of CO and CO_2 corresponded to final concentrations in the reaction system of around 10% each (Table 5.6) compared to values of around 2.5 and 1.5% respectively in the single pass reaction mode (Table 5.2).

Following this the reactor was pressurized to 32 atm with methane and oxygen, at the 10% concentration level. The reactor gas flow rate was set at 200 mL/min (NTP) (12s reaction volume^{-1} NTP). The reactor temperature was raised to the point where all of the reactant oxygen was consumed, operating in the single pass (once through) mode.

Once a steady state was reached the reactor gas was directed into the Recycling system by closing S1 and opening valve A. The pressure was allowed to build to 27 atm before operating the Gas Booster to pressurize the Recycle Gas in the Recycle Gas Storage Cylinder (RGSC). Methanol and water and any other condensibles were removed from the gas stream by the two condensers. On reaching a pressure of 34 atm (Heiss gauge) the Recycle Gas was introduced into the main stream feed CH_4 by careful adjustment of the appropriate control valves, i.e. the Recycle Gas Control Valve (RGCV) and Methane Gas Control Valve (MGCV), while keeping the Reactor pressure (meter) constant (Figure 5.1) to give a mixed feed of Recycle and input methane gas.

The gas from the Reactor and Recycle systems was sampled and analyzed independently by gas chromatography. The methanol yield was

monitored as a function of Recycle which depended on the operation of the Gas Booster.

CO and CO_2 levels were also monitored closely, from both the Recycle and Reactor gas sytems. Recirculation was complete when these components reached similar levels in both systems, i.e. distributed homogeneously throughout.

The condensers were maintained at -50 to -60°C using liquid nitrogen.

The experiment was run for a total of eleven hours and twenty-two minutes (Reaction Time) and Recycling occupied seven hours and forty-two minutes. The Gas Booster was operated ten times during this latter period to give an average recycle flow of 175 mL/hr.

RESULTS AND DISCUSSION

(i) Recirculation IV

The Reactor Gas in the single pass and recycle modes was sampled and analysed at various intervals throughout the experiment for all reaction products, and the data has been tabulated (Tables 5.1-5.7).

The Recycle Gas (gas from the Recycle System) was analysed for the presence of water and methanol, levels of which were found to be very low (<0.1%) (Table 5.7). Both CO and CO_2 levels relative to nitrogen were monitored and compared with those determined in the reactor gas (Table 5.8).

Since the initial concentrations of both CO and CO_2 (7-10%) in the recycle system were greater than that produced reactively (1-2%), as they were artificially created, recycling was assumed to be complete

when the levels in the Recycle and Reactor systems reached parity. As methanol and water were effectively removed by the condensers, the CO and CO_2 levels were expressed relative to the reactant nitrogen level rather than absolute percentage concentrations for the sake of comparisons.

The change in CO and CO_2 levels have been expressed in the form of a CO/CO_2 ratio variation with time (Figure 5.2). In the Reactor system the CO/CO_2 ratio increased to over 1.6 and began to fall as the reactor gas was admitted to the Recycle system. The ratio remained steady at 1.40 until recirculation commenced whereupon it fell before levelling off at a value of 0.7. It appeared therefore that CO is favoured in the single pass reaction mode and CO_2 in the recycle mode. This is probably due to oxidation of recycled CO in the reactor.

The levels of CO and CO_2 in the Recycle and Reactor Gas reached equilibrium (CO/CO_2 ratio 0.7 - 0.8) after a two hour recycle period (average recycle rate = 175.4 mL/hr = 4.5 reaction volumes) and thus the system had undergone complete recirculation. Recirculation was continued for a further four hours.

Because of the high product concentrations of CO and CO_2, caused by their artificial introduction into the system, variation in the yield of methanol produced with time was expressed relative to the amount of methane consumed. This ratio was determined from the respective molar amounts of methanol and methane relative to nitrogen (av. value = 0.021 yield 2%) (Table 5.10). This trend has been displayed graphically in Figure 5.3. The yield of methanol decreased (1%) upon admission of the reactor gas to the Recycle System and still further when recycling began. The equivalent single pass yield of methanol was restored after

three hours recycling (av. value = 2.1%). Given sufficient time therefore to allow the production of methanol to recover, during the single pass to recycling mode transition, it appeared that the yield of methanol returned to its 'single pass' value in spite of quite high levels of CO and CO_2 in the system.

CONCLUSION

The results from this study indicate, at the bench scale, that carbon monoxide and carbon dioxide do not detectably interfere with the production of methanol under recycle conditions, at O_2 concentration levels of 10%.

Though the yield decreased from 2% upon initiation of recirculation to 1% it was fully restored with continued operation (Figure 5.3).

EXPERIMENTAL PROCEDURE - Recirculation V

The Recycle System was pressurized with CO_2 (1.4 atm) and CO (2.0 atm) to 3.4 atm. Methane was added to give a final pressure of 510 psig. This procedure differed from that in the previous recirculation experiment in two ways: (1) The amounts of CO and CO_2 in the system were less, (2) The addition of methane alone to reactor pressure.

The amounts of CO and CO_2 corresponded to concentrations of 2.8 and 2.0% in the Reactor Gas upon Recycle (Table 5.12) compared to values of 1.2 and 0.7% respectively in the single pass Reaction mode (Table 5.11).

The Recycle System was made into a closed loop at attaching a length of tubing connecting valve C to valve A. The contents of the Recycle System were recirculated using the gas booster to ensure good mixing.

The addition of methane in this way meant once a steady state reaction condition had been reached in the reactor, that upon admission of the reactor gas to the Recycle System, recirculation could begin almost immediately.

A concentration level of 4.5% O_2, in reactant methane feed, was used in this experiment, to achieve higher initial methanol selectivity.

The remaining experimental procedure was similar to that in the previous Recirculation experiment with the additional facility of now being able to sample the recycle/main feed mixture due to the installation of a sampling line and valve just prior to the entrance of the reactor (S4-Figure 5.4).

The condensers were kept at -55 to -60°C using dry ice-ethanol.

RESULTS AND DISCUSSION

Both the Reactor and Recycle (system) gases were analysed at various intervals and particular attention was paid to the change in CO, CO_2 and methanol levels with time (Tables 5.11-5.16). The level of CO_2 increased with time as would be expected (Table 5.17). This observation was reflected in the change in CO/CO_2 ratio with time in the Recycle and Reactor Gas analyses (Table 5.18).

Since the Reactor Gas and Recycle Gas CO and CO_2 levels were not too dissimilar to start with anyway, their convergence could not be used as an indication of the degree of Recirculation.

Based on the previous Recirculation however, the system was assumed to have undergone complete recycle in two hours.

Since the artificially introduced CO and CO_2 was similar in concentration to that produced in the reactor, and the buildup with time was relatively small, it was considered reasonable to compare the change in methanol selectivity with time on the basis of the values determined directly from analysis (Tables 5.11-5.16).

The variation of methanol selectivity with time is shown in Table 5.19. The values are all very low considering the level of O_2 employed would normally return selectivity in the region of 70-80%. The production of formaldehyde obviously would reduce this value but this still meant that the methanol selectivity was low.

Comparison of the methanol selectivities (Table 5.20), based on consumed methane in the combined Recycle/Main CH_4 gas feed, showed that the values were between 55 and 60% during Recirculation. This

improvement compared with the single pass value was due to the lesser yields of formaldehyde (~20% selectivity) produced during recirculation.

Because of the presence of artificially introduced CO and CO_2 with the system it meant that selectivities based on oxidized product concentrations could not be used (Eqn. (2) - Part One). The methanol yield was determined on the basis of the molar ratio of methanol relative to N_2 as determined by g.c.

Recycle Mode

$$\text{Conversion } CH_4 = \frac{\frac{CH_4}{N_2} \text{ in (Mainfeed } CH_4 + \text{Recycle } CH_4) - \frac{CH_4}{N_2} \text{ out}}{\frac{CH_4}{N_2} \text{ in (Main feed } CH_4 + \text{Recycle } CH_4)} \quad (1)$$

$$\text{Selectivity } CH_3OH = \frac{\text{yield } CH_3OH}{\text{conversion } CH_4} = \frac{\text{\%mole area } CH_3OH/N_2}{\text{conversion } CH_4} \quad (2)$$

In order to do this the reactant CH_4/N_2 ratios in the combined Recycle/Main CH_4 gas feed by sampling the feed prior to the reactor. The CH_4/N_2 ratios were determined experimentally by sampling the input main CH_4 feed, the combined Recycle/Main CH_4 feed and the reactor gas (Tables 5.13-5.15). The CH_4/N_2 ratio was higher in the Recycle/Main CH_4 feed and decreased in the recycle gas due to the increasing concentration of N_2 as CH_4 was consumed.

Significantly methanol selectivity did not change appreciably upon recirculation with CO and CO_2 in the recycle feed.

CONCLUSION

These results again indicate that the reaction proceeds to methanol unhindered by CO and CO_2 at low to intermediate levels (2-4%). The inference is that recirculation of CO and CO_2 through the reactor together with unreacted CH_4 does not affect the conversion to methanol at these levels.

EXPERIMENTAL PROCEDURE - 1. Restoration of Methanol Selectivity

2. Recirculation VI

1. Restoration of methanol selectivity to 70-80% at 5% 0_2 concentration.

The reactor system was completely overhauled from the inlet feed lines to the exit needle control valve in an attempt to improve on the low methanol selectivity values recorded in the previous Recirculation experiments. The glass liner was replaced and new stainless steel fittings were substituted for brass where possible. The input line from the trap used to introduce sensitizers into the reactant gas streams was completely flushed with solvent and evacuated in case any sensitizer residues were interfering with the reaction. The mixing cross (brass) was replaced (extensive corrosion caused by 0_2) with a steel one and the mixing section repacked with Teflon turnings.

The exit line was replaced as it was suspected that some loss of methanol may be occurring here through adsorption by higher hydrocarbon residues. The line was rewrapped with heating tape and insulated carefully to prevent hot spots, determined by inserting a thermocouple at various points along its length. The exit line temperature was maintained at around 100°C to prevent the possibility of methanol decomposition.

The temperature of the exit gas heater was reduced to 180°C for similar reasons although here the temperature could not be reduced too much for fear of condensation particularly at the exit needle control valve since the gas leaves the heated reaction zone at between 350 - 400°C.

The degree of reactant mixing was also checked and found to be satisfactory.

All of these adjustments afforded some small improvement in CH_3OH selectivity but the major improvements came with optimization of reaction temperature, flow rate and improvements to the gas chromatographic system.

Considerable improvement to the detection of the higher boiling products was made by installing the G.C. oven thermocouple within the oven itself. Previously the thermocouple was mounted next to the heating filament presumably for more precise isothermal operation. However, lately in this situation the temperature indicated was often some 50°C higher than the true temperature and was not reproducable for the same temperature setting. Installation of the sensing thermocouple inside the G.C. oven ensured a more accurate indication of column temperature at the expense of heating response. Peak shapes particularly of water and methanol were sharpened leading to reduced integration error.

It was also found that broadening of the peaks, again particularly the higher boiling components, increased using the dual column system as would be expected based on increased column length. This broadening was offset and peaks sharpened by analysing on one column at a time until the dual column conditions could be improved.

Porapak Q was more efficient in terms of reduced peak broadening compared to Porapak T, though the 'T' column had probably deteriorated due to considerable use.

The separation of O_2, N_2, CH_4, and CO was carried out independently on Molecular Sieve 5A.

With these improvements to the analytical system it was now possible to objectively determine and measure the effects of reaction parameters on the yield and selectivity of methanol.

A systematic study was carried out wherein the reaction temperature, length heated reaction zone, reaction flow rate and degree of oxygen consumption were varied and the response of the reaction monitored.

2. Recirculation VI

With the improvements to the system it was considered that the effects of high CO and CO_2 concentrations in the reactant feed at high methanol selectivity could be studied.

The recycle system was charged with CO_2 to 4.8 atm and CO to 10.3 atm (P = 5.5 atm) and to 39 atm with CH_4. This gas was recirculated within the recycle system to effect thorough mixing. Upon recirculation through the reactor system these levels of CO and CO_2 corresponded to 7.6% and 8.2% of the input Recycle and Methane feed (Table 5.27).

The Reactor system was isolated from the Recycle system and pressurized with reactant feed (CH_4 + O_2) to 37 atm with an O_2 concentration level of 2.9% at a reactor flow rate of 150 mL/min NTP.

Once the reaction had reached steady state at 317°C reactor gas was admitted to the Recycle system. Upon reaching reactor pressure the Recycle gas was allowed to mix with the input methane feed and recirculation commenced.

Throughout the course of the experiment analysis of the Recycle Gas, Reactor Gas and Recyle and input CH_4 gas were made in order to be

able to determine the C/N_2 ratios pertaining to the feed and the reactor gas so as to allow determination of the conversion and methanol selectivity.

RESULTS AND DISCUSSION

1. Restoration of methanol selectivity

The effects of exit line (post flow control valve) and the exit heater (pre-flow control valve) temperature were studied as a function of methanol peak height with several injections being made, as, N_2 could not be separated and used as reference at the high isothermal G.C. temperature required to elute methanol (Table 5.21).

Just prior to the remainder of the experimental results described here a new methane cylinder was installed and found to contain 0.09% ethane which was sufficient to effect a substantial reduction in reaction temperature. The increase in methanol selectivity (53 - 58%) with reduction in reaction temperature (367 - 349°C) is shown in Table 5.22.

The selectivity generally increased with reduction in reaction temperature. Evidently methanol production is favored by lower reaction temperatures minimizing formation of CO and CO_2. It was also observed that it made little difference to the selectivity whether a 45 or 35 cm heated reaction zone was used though a 10 cm heated zone proved wholly inadequate in terms of methanol production at the range of flow rates (100-150 mL/min NTP) and temperatures (306-415°C) studied. Thus a minimum heated zone of between 10 and 35 cm (9 - 30 mL) was required to initiate the reaction to methanol.

The effect of reactor flow rate on methanol selectivity is shown in Table 5.23. The selectivity optimized at 63% at 143 mL/min (NTP).

It had been suggested that the selectivity of methanol increased when not all of the available reactant O_2 was consumed. Accordingly an experiment was conducted at a temperature (310°C) at which O_2 was incompletely consumed and the effect of reactor flow rate studied (Table 5.24). The value of methanol selectivity increased slightly but most likely due to the effective lower concentration of O_2 consumption rather than its presence in the reaction mixture. The most important observation here was the optimization of the methanol selectivity (64-65%) over the Reactor flow rate range of 120-166 mL/min.

2. Recirculation VI

The Recirculator was run for a total of 7 hours during which time 1100 mL (NTP) of recycle gas was pumped through the reaction system (heated reaction zone volume = 30 mL = 35 cm length reactor tube). Analysis of the reactor gas in the single pass mode is given in Table 5.25.

Values of the input C/N_2 (reactant CH_4/N_2), in the combined Recycle and methane feed, and output C/N_2 (product CH_4/N_2, in the reactor gas, were measured, by G.C., to determine the conversion and methanol selectivity (Table 5.26). The compositions of the Recycle-Main feed and Reactor Gas upon Recycle are shown in Table 5.27 and 5.28.

All but one of the differences (conversion) (Table 5.26) between the input and output CH_4/N_2 values were negative. This reflected the inaccuracy in measuring a small value for N_2 at a low conversion level

where the slightest error in this value significantly altered the CH_4/N_2 ratio.

One estimate of the selectivity was made however by applying the same N_2 value found in the input analysis to the output analysis. This estimate, 77%, indicated that even high CO/CO_2 (7/12% of recycle feed - Table 5.28) concentrations did not influence the methanol selectivity. The analysis of the reactor gas products indicated qualitatively (CH_3OH peak area) good methanol selectivity but could not be quantified due to difficulty in measuring N_2 precisely. This affected both the conversion and selectivity values since their determination are expressed relative to N_2 (eqns. 1 and 2 this section).

EXPERIMENTAL PROCEDURE - Recirculation VII

In an attempt to offset the error in measuring C/N_2 ratios the N_2 concentration in the methane supply cylinder was increased (Table 5.29). Two experiments were envisaged at this stage. In the first the reactant O_2 concentration would be high 10% to ensure measurable conversion (Recirculation VII). In the second the reactant O_2 concentration would be low 4% to ensure high methanol selectivity (Recirculation VIII). In the first of these two studies the O_2 concentration was increased to 9%.

The Recycle system was charged with CO to 4.8 atm, with CO_2 to 9.6 atm and to 27 atm with CH_4. These amounts corresponded to concentration levels of 16% each for CO and CO_2 in the Recycle gas prior to recirculation (Table 5.30) and levels of 7 and 14% respectively in the Reactor gas (inclusive of reaction)(Table 5.33).

RESULTS AND DISCUSSION

Product analysis of the reaction gas for the reactor operating in the single pass mode is given in Table 5.29. The conversion was calculated on the basis of carbon in the oxidation products but a more precise value was found based on methane consumption, (CH_4/N_2 reactants - CH_4/N_2 products) as detailed in Recirculation V (Eqn. (1)), averaged over several determinations (Table 5.31).

Once Recirculation was underway the combined Recycle-Main feed gas CH_4/N_2 ratio was determined followed by analysis of the Reactor gas to estimate the same parameter and hence the conversion (Table 5.32). The reactor gas was also analysed to determined the average product

composition (Table 5.33). The value of the methanol selectivity in this Table was based on the ratio of the product CH_3OH/N_2 (yield) (0.29) relative to the CH_4 consumed (conversion) (9.533 - 8.914 = 0.619 CH_4/N_2, Table 5.32), assuming CH_4 was converted solely to oxidized carbon product. The selectivity value of 47% returned during Recycle compares favourably with the value of 43% prior to Recycle.

CONCLUSION

The results of Recirculation VII underline the conclusions drawn from Recirculations IV and V that CO and CO_2 recycled in amounts less than 20% of the input reactant gas do not interfere with the formation of methanol.

EXPERIMENTAL PROCEDURE - Recirculation VIII

The O_2 concentration was set at 3.4% prior to the experiment. The Recycle system was charged with CO_2 to 5.8 atm and CO to 10.3 atm and finally with CH_4 (containing N_2) to 27.4 atm. These amounts corresponded to concentration levels of 16% for CO and 20% for CO_2 in the Recycle gas prior to recirculation (Table 5.34) and of 6% and 21% respectively in the Reactor gas (Table 5.38) following reaction.

The Reactor flow rate (RFR) was set at 40 mL/min (NTP)(S.T. = 1074s) a much reduced flow compared to previous Runs (160 - 100 mL/min; 200 - 300s). It was found that at lower O_2 concentrations ($\ll$5%) that the methanol selectivity was optimum at between 40-60 mL/min flow (NTP) and at an MTCR of around 315°C using the CH_4 containing ~ 0.1% ethane.

This lower flow rate however increased the time required to replenish the Recycle system from the Reactor system during Recirculation.

RESULTS AND DISCUSSION

The input CH_4/N_2 ratio prior to reaction and the output CH_4/N_2 values with the reactor operating in the single pass mode were determined (Table 5.35). The CH_4 conversion was estimated based on the difference between these two levels. Operating in the single pass mode the methanol selectivity was determined at 70% (Table 5.36) based on oxidized carbon assuming complete conversion of reactant carbon (CH_4) to produce carbon in the oxidized species (CO, CO_2 and CH_3OH).

The reactor gas was admitted to the Recycle system to bring it to reactor pressure. Once this level was reached the Recycle gas was allowed to mix with the Main feed CH_4 and flow into the reactor whereupon recirculation commenced. After some time the combined Recycle - Main feed gas was sampled to determine the input CH_4/N_2 ratio. The Reactor gas was similarly sampled to determine the output CH_4/N_2 ratio from which the conversion could be estimated (Table 5.37).

The Reactor gas was further analysed to determine the product composition (Table 5.38) from which the methanol/N_2 ratio could be evaluated during Recycle.

This ratio permitted the methanol selectivity, during Recycle (with artificially produced levels of CO and CO_2 in the reactor), to be determined based on the consumed CH_4/N_2 (Table 5.37) assuming the input CH_4 was converted solely to oxidized product.

The value of 63% was a little lower than that found while operating in the single pass mode. However, analysis of the input reactant stream both during and after recycle showed that the reactant O_2 concentrations had increased from the initial set value of 3.4% to 6% due to a gradual decrease in methane pressure during the course of the Run with the onset of Recycle, i.e. Recycle-Main feed CH_4 pressure slightly less than original Main feed only CH_4 pressure. With this in mind one would expect a decrease in methanol selectivity as was observed and the methanol selectivity values prior to and during Recycle are therefore comparable.

CONCLUSION

In spite of high concentrations of CO and CO_2 (initially comprised 35% of recycle feed, Table 5.34) methanol was still produced in good selectivity (60%) during recirculation (Table 5.38). The selectivity can be considered to better than this if one allows for the higher O_2 concentrations in the reactant feed encountered towards the final stages of the Run when the selectivity was determined. This experiment showed that at good methanol selectivity (70%) (obtained by operating at low O_2 (<4%) and low conversion (<5%)) the formation of methanol was not appreciably affected by the presence of high concentrations of CO and CO_2 (25% of reactor gas). This is an important factor to be considered for the scale up of the design to the pilot or industrial scale level. Essentially CO and CO_2 produced by the oxidation reactor need not be removed (by purging) and as such conserves valuable feedstock (Natural gas or methane) which will reduce the overall operating costs. Operating at low conversion and high methanol selectivity the reaction yields of CO and CO_2 are low (2% total) and therefore under these conditions Recirculation could continue for considerable time before CO and CO_2 built up to levels of 30% total.

RECIRCULATION IV

Table 5.1. Oxidation of CH_4 with O_2 - Single Pass Mode

Time of Analysis - 12:10

Pressure = 34.0 atm Reactor Temp. = 450°C

Reactor Flow Rate = 11.7s(reac. vol)$^{-1}$NTP % $[O_2]$ = 9.91 ± 0.26

Space Time (S.T.)(Reactor) = 151s(reac. vol)$^{-1}$

	O_2	N_2	CO_2	CH_4	CO	H_2O	CH_3OH
% Area (molar)		1.30	1.71	85.10	2.30	6.80	1.96
% Selectivity			18.04		38.48		32.83
C/N_2			1.32	65.53	1.77		1.51
O_2/N_2			1.32		0.88	2.62	0.75

% Conversion = 6.56 % C. bal = 103.50

% Yield = 2.15

Table 5.2. Oxidation of CH_4 with O_2 - Single Pass Mode

Time of Analysis = 13:03

Pressure = 32.5 atm Reactor Temp. = 414°C

RFR = 11.7s (reac. vol)$^{-1}$ NTP % [O_2] = 9.91

S.T.(reactor = 151s(reac. vol)$^{-1}$

	O_2	N_2	CO_2	CH_4	CO	H_2O	CH_3OH
% Area		0.96	1.46	85.83	2.40	7.39	1.96
% Selectivity			25.00		41.18		33.80
C/N_2			1.13	66.80	1.86		1.526
O_2/N_2			1.13		0.93	2.875	0.76

% Conversion = 6.33 % C. bal = 105.30

% Yield = 2.14

Table 5.3. Oxidation of CH_4 with O_2 - Single Pass Mode

Time of Analysis = 16:55

Pressure = 35 atm Reactor temp. = 414.5°C

RFR = 11.7s(reac. vol)$^{-1}$ NTP % [O_2] = 9.91

S.T.(reactor) = 151s(reac. vol)$^{-1}$

	O_2	N_2	CO_2	CH_4	CO	H_2O	CH_3OH
% Area		0.75	1.23	88.71	1.76	5.80	1.75
% Selectivity			25.96		37.16		36.87
C/N_2			0.915	65.85	1.31		1.30
O_2/N_2			0.915		0.65	2.15	0.65

% Conversion = 5.10 % C. bal = 102.47

% Yield = 1.88

Table 5.4. Oxidation of CH_4 with O_2 - Recycle Mode (Reactor Gas Analysis)

Time of Analysis = 20:15

Pressure = 34.3 % $[O_2]$ = 9.91

Reactor Temp. = 414°C

	O_2	N_2	CO_2	CH_4	CO	H_2O	CH_3OH
% Area		2.28	9.38	76.10	7.32	4.10	0.82
% Selectivity			53.55		41.78		4.67
C/N_2			6.87	55.00	5.36		0.60
O_2/N_2			6.87		2.68	1.50	0.30

Table 5.5. Oxidation of CH_4 with O_2 - Recycle Mode (Reactor Gas Analysis)

Time of Analysis = 20:51 % $[O_2]$ = 9.91

Pressure = 34.3 atm Reactor Temp. = 412°C

	O_2	N_2	CO_2	CH_4	CO	H_2O	CH_3OH
% Area		1.95	10.10	72.81	8.19	5.42	1.52
% Selectivity			50.98		41.33		7.67
C/N_2			7.77	56.00	6.30		1.17
O_2/N_2			7.77		3.15	2.08	0.58

Table 5.6. Oxidation of CH_4 with O_2 - Recycle Mode (Reactor Gas Analysis)

Time of Analysis = 21.08 % $[O_2]$ = 9.91

Pressure = 34.3 atm Reactor Temp. = 413°C

	O_2	N_2	CO_2	CH_4	CO	H_2O	CH_3OH
% Area		1.73	10.53	70.02	9.71	7.45	1.60
% Selectivity			50.63		41.71		7.65
C/N_2			7.77	51.66	6.40		7.65
O_2/N_2			3.88		3.20	2.75	0.58

Table 5.7. Oxidation of CH_4 with O_2 - Recycle Mode (Recycle Gas Analysis)

Time of Analysis = 17.47 % $[O_2]$ = 9.91

Pressure = 33.03 atm Reactor Temp. = 413°C

	O_2	N_2	CO_2	CH_4	CO	H_2O	CH_3OH
Area(molar)		30	165.4	3660	232	s	v.s.
C/N_2			2.75	61.00	3.86		

Table 5.8. Oxidation of CH_4 with O_2 - Levels of CO and CO_2 in Recycle Gas System

Pressure atm	Temp. °C	CO/N_2	CO_2/N_2	Time of Analysis
33.03	413	1.4	1.93	17.47
32.86	414.5	3.8	4.0	18.54
32.86	414.5	3.6	3.7	19.20
33.45	411.5	9.3	6.2	22.05
33.45	411.5	9.3	6.4	22.28
31.33	411	9.0	6.2	22.40

Table 5.9. Oxidation of CH_4 with O_2 - CO/CO_2 ratio

I(a) Single pass mode - Reactor Gas

Pressure = 33 atm Reactor Temp. = 414°C RFR = 11.7s(reac. vol.)$^{-1}$

Time of Analysis	Elapsed Time (min) (from steady state)	CO/CO_2 (molar ratio)
12:10	50	1.3
13:03	103	1.6
14:48	208	1.4
16:55	335	1.4

(b) Recycle Mode - Reactor Gas

Pressure = 34 atm Reactor Temp. = 413°C

18:54	454	1.07
20:15	540	0.78
20:51	571	0.81
21:08	588	0.82
22:35	675	0.65

Table 5.9 (cont'd...)

II. Recycle Mode - Recycle Gas

Pressure = 34 atm Reactor Temp. = 413°C

Ratio of CO/CO_2 at time zero up to initiation of recirculation = 1.60

Time of Analysis	Elapsed Time (min) (from steady state)	CO/CO_2 (molar ratio)
17:47	387	1.40
19:20	480	1.02
22:05	645	0.67
22:28	668	0.69
22:40	680	0.69

Table 5.10. Oxidation of CH_4 with O_2 - Methanol Yield

a) Single pass mode - Reactor Gas

Pressure = 33 atm Reactor Temp. = 414°C

RFR = 11.7s (reac. vol)$^{-1}$ $[O_2]$ = 9.91%

Time of Analysis	Elapsed Time (min) (from steady state)	$\frac{CH_4}{N_2}$	$\frac{CH_3OH}{N_2}$	$\frac{CH_3OH}{CH_4}$	% Yield CH_3OH
12:10	50	65.33	1.51	0.0230	2.15
13:03	103	66.80	1.526	0.0228	2.14
14:48	208	65.33	1.262	0.0193	-
16:55	335	65.85	1.30	0.0197	1.88
b) Recycle Mode - Reactor Gas					
20:15	535	55.00	0.60	0.011	1.00
20:51	571	56.00	1.17	0.0208	2.02
21:08	590	51.66	1.17	0.0227	2.20

RECIRCULATION V

Table 5.11. Oxidation of CH_4 with O_2 - Single Pass Mode

a) Reactor Gas

Time of Analysis = 11:40 Reactor Temp. = 411°C

Reactor Flow Rate = 12.5s(reac. vol)$^{-1}$ NTP

Pressure = 35.5 atm

S.T.(reactor) = 191s % $[O_2]$ = 4.54

	O_2	N_2	CH_4	CO	CO_2	HCHO	H_2O	CH_3OH
% Area(molar)		9.94	87.43	1.17	0.68	3.00	5.33	1.46
% Selectivity				19.37	11.26	49.67		23.18
C/N_2			84.00	1.12	0.65	2.87		1.40
O_2/N_2				0.56	0.65	1.43	2.56	0.70

% conversion = 6.71 % C. bal = 100.04

% yield = 1.55

Input Reactant Gas CH_4/N_2 = 90.00

b) Recycle Gas C/N_2 Values Time of Analysis = 11:39

	CH_4	CO	CO_2
C/N_2	78.67	2.20	1.67

Table 5.12. Oxidation of CH_4 with O_2 - Recycle Mode

a) Reactor Gas

Time of Analysis = 12:43 % $[O_2]$ = 4.54

Pressure = 35.6 atm. Reactor Temp. = 411°C

	O_2	N_2	CH_4	CO	CO_2	H_2O	CH_3OH
% Area		1.04	83.15	2.80	1.94	8.91	2.17
% Selectivity				30.90	21.50		24.04
C/N_2			79.51	2.66	1.85		2.07
O_2/N_2				1.33	1.85	4.26	1.03

% conversion = 7.64 % C. bal = 95.65

% yield = 1.84

b) Recycle Gas Time of Analysis = 12:33

	CH_4	CO	CO_2
C/N_2	83.50	2.25	1.32

Table 5.13. Oxidation of CH_4 with O_2 - Recycle Mode

a) Reactor Gas

Time of Analysis = 13.57 % $[O_2]$ = 4.54

Pressure = 35.5 atm Reactor Temp. = 411°C

	O_2	N_2	CH_4	CO	CO_2	H_2O	CH_3OH
% Area		1.33	91.24	3.47	2.01	6.66	2.07
% Selectivity				45.94	26.71		27.50
C/N_2			76.05	2.89	1.68		1.73
O_2/N_2				1.45	1.68	2.77	0.86

% Conversion = 7.63 % C. bal = 91.60

% Yield = 2.10

b) Recycle Gas Time of Analysis = 13.20

	CH_4	CO	CO_2
C/N_2	72.44	2.60	1.58

c) Reactant + Recycle Feed Gas Time of Analysis = 15.25

	CH_4	CO	CO_2
C/N_2	79.01	1.33	0.55

Table 5.14. Oxidation of CH_4 with O_2 - Recycle Mode

a) Reactor Gas

Time of Analysis = 15:48 % $[O_2]$ = 4.54

Pressure - 35.4 atm Reactor Temp. = 412°C

	O_2	N_2	CH_4	CO	CO_2	HCHO	H_2O	CH_3OH
% Area	-	1.10	75.72	2.86	2.76	1.83	13.92	1.81
% Selectivity				32.38	29.80	19.83		19.47
C/N_2			69.00	2.60	2.51	1.67		1.64
O_2/N_2				1.30	2.51	0.83	6.33	0.82

% Conversion = 10.87 % C. bal = 86.02

% Yield = 2.12

b) Recycle Gas Time of Analysis = 15:42

	CH_4	CO	CO_2
C/N_2	80.25	2.67	2.79

c) Reactant + Recycle feed gas

	CH_4	CO	CO_2
C/N_2	79.75	2.00	1.85

Table 5.15. Oxdiation of CH_4 with O_2 - Recycle Mode

a) Reactor Gas

Time of Analysis = 16:56 $\%[O_2]$ = 4.54

Pressure = 35.5 atm Reactor Temp. = 411°C

	O_2	N_2	CH_4	CO	CO_2	HCHO	H_2O	CH_3OH
% Area	-	1.06	78.01	3.00	2.84	2.72	10.63	1.75
% Selectivity				27.05	25.83	24.63		22.51
C/N_2			73.33	2.80	2.67	2.55		2.33
O_2/N_2				1.40	2.67	1.67	5.00	1.16

% Conversion = 12.36 % C. bal = 93.00

% Yield = 2.78

b) Recycle Gas Time of Analysis = 16:45

	CH_4	CO	CO_2
C/N_2	65.65	2.54	2.42

c) Reactant + Recycle feed gas

	CH_4	CO	CO_2
C/N_2	76.30	1.78	1.68

Table 5.16. Oxidation of CH_4 with O_2 - Recycle Mode

a) Reactor Gas

Time of Analysis = 17:54 % $[O_2]$ = 4.54

Pressure = 35.5 atm Reactor Temp. = 412°C

	O_2	N_2	CH_4	CO	CO_2	H_2O	CH_3OH
% Area	-	0.98	67.17	1.96	2.61	10.43	1.68
% Selectivity				28.13	37.55		34.32
C/N_2			68.67	2.00	2.67		2.44
O_2/N_2				1.00	2.67	5.33	1.22

% Conversion = 9.38 % C. bal = 84.20

% Yield = 3.22

b) Recycle Gas Time of Analysis = 18:32

	CH_4	CO	CO_2
C/N_2	78.75	3.37	3.75

Table 5.17. Oxidaton of CH_4 with O_2: Variation of CO/N_2 and CO_2/N_2 ratios with Time

Pressure = 35.6 atm Temp. (reactor) = 410°C

Time of Analysis	Time Interval from Start of Recycle	CO/N_2*	CO_2/N_2
11:39	0	2.20	1.67
12:33	54	2.25	1.32
13:20	121	2.60	1.58
15:42	243	2.67	2.79
16:45	306	2.54	2.42
18:32	413	3.37	3.75

*These ratios are initial. higher than those in Table 5.8 because the concentration of N_2 in the feed was less.

Table 5.18. Oxidation of CH_4 with O_2: Variation of CO/CO_2 ratio with time.

I(a) Single pass mode - Reactor Gas

Pressure = 35 atm Temp. = 410°C RFR = 12.5s(reac. vol)$^{-1}$ NTP

Time of Analysis	Elapsed Time (min) (from Steady State)	CO/CO_2 (molar ratio)
11:40	60	1.77
(b) Recycle Mode - Reactor Gas		
12:43	123	1.44
13:57	197	1.72
15:48	308	1.036
16:56	366	1.040
17:54	434	0.75
II. Recycle Mode - Recycle Gas		
11:39	59	1.32
12:33	117	1.70
13:20	160	1.64
15:42	302	0.85
16:45	365	1.05
18:32	472	0.89

Table 5.19. Oxidation of CH_4 with O_2 - Methanol Selectivity as determined from analyses of reactor gas.

a) Single Pass Mode - Reactor Gas

Time of Analysis	Elapsed Time (min) (from steady state)	% Methanol Selectivity
11:40	60	23.18

b) Recycle Mode - Reactor Gas

12:43	123	24.04*
13:57	197	27.50*
15:48	308	19.47
16:56	366	22.51
17:54	434	34.32*

*HCHO not detected

Table 5.20. Oxidation of CH_4 with O_2. Methanol selectivity based on conversion of CH_4 in Recycle and Main Feed gas input feed.

Time of Analysis	Reactor Input (Recycle/Main Feed CH_4) CH_4/N_2	Reactor Output (Reactor Gas) CH_4/N_2	Conversion CH_4/N_2	%Yield CH_3OH	%Selectivity CH_3OH
13:57	79.01	76.05	2.96	2.10	71.0
15:48	79.75	76.54	3.21	1.81	56.38
16:56	76.30	73.33	2.97	1.75	58.92

% selectivity CH_3OH determined from equation (2):

$$= \frac{CH_3OH \text{ yield}}{\text{conversion } CH_4} \times 100$$

$$= \frac{\text{molar area } CH_3OH/N_2}{\text{molar area } CH_4/N_2 \text{ converted}} \times 100 - \text{(by g.c. corrected for sensitivity)}$$

$$= \frac{175}{2.97} \times 100$$

$$= 58.92$$

Table 5.21. The effect of reaction exit line and exit heater temperature methanol yield.

O_2 conc. = 3.34%. Pressure = 35 atm Reactor Flow = 181mL/min (NTP)

Conditions (Temp.°C)	CH_3OH peak height (cm)
exit line = 110 exit heater = 201 Reaction zone = 427	1.90
exit line = 110 exit heater = 201 Reaction zone = 407	2.05
exit line = 30 exit heater = 201 Reaction zone = 407	2.10
exit line = 30 exit heater = 169 Reaction zone = 407	2.25
exit line = 73 exit heater = 140 Reaction zone = 403	2.40

Table 5.22. Optimization of CH_3OH selectivity with Reaction Temperature.

O_2 conc. = 3.53% Pressure = 33.5-36.8 atm. Reactor Flow = 177-200 mL/min (NTP).

Reaction Temperature °C (35 cm zone)	% CH_3OH selectivity
370	55.50
367	52.80
359	57.62
349	58.20
340	55.46

Table 5.23. Optimization of CH_3OH selectivity with Reactor Flow Rate (NTP).

O_2 Conc. = 3.53% Reactor temp. = 340°C (35 cm zone)

Reactor Pressure = 33.7 - 37.0 atm.

Reactor Flow Rate (mL/min)	$\%CH_3OH$ selectivity
48	50.00
88	58.80
120	59.00
143	62.95
176	55.46

Table 5.24. Optimization of CH_3OH selectivity with Reactor Flow Rate in presence of Oxygen (incomplete consumption of reactant oxygen).

Initial O_2 conc. = 4.16%. Frac. consumed = 0.60 at 167 mL/min - 0.75 at 88 mL/min.

Reactor Pressure = 35 - 37.5 atm Reactor temperature = 310°C (35 cm zone)

Reactor Flow Rate (mL/min. NTP)	$\%CH_3OH$ selectivity
43	33.75
81	60.81
88	58.80
96	52.87
107	55.74
111	59.44
120	63.77
136	63.30
150	64.41
166	65.14
200	61.78

RECIRCULATION VI

Table 5.25. Oxidation of CH_4 - Single pass mode.

Reactor pressure = 38 atm. $\%O_2$ conc. = 2.82

Reactor temperature = 317°C Reactor Flow Rate = 19.5s(reac. vol)$^{-1}$

	O_2	N_2	CO	CH_4	CO_2	H_2O	CH_3OH
molar %	-	2.19	1.02	90.12	0.23	4.56	1.87
% Selectivity			32.0		7.3		60.0
C/N_2			0.466	41.18	0.104		0.856
O_2/N_2			0.233		0.104		0.423

% Conv. = 3.35 % C. bal = 86.20

% Yield = 2.06

Table 5.26. Values of conversion (CH_4), yield and selectivity (methanol) determined during Recirculation.

Reactor Pressure = 38 atm Reactor Temp. = 317 ± 1°C

Time of Analysis	input CH_4/N_2	output CH_4/N_2	% Conversion CH_4	% Yield CH_3OH	% Selectivity CH_3OH
12:00			3.35	2.06	60.0
13:33	33.3	38.1			
14:46	31.6	34.6			
15:36	31.5	38.4			
16:30	35.0	37.5			
17:42	29.4	26.1	3.29	2.55	77.51
18:23	32.4	31.2	1.2	1.65	

Table 5.27. Composition of combined Recycle-Main CH_4 feed

Feed press = 38 atm

Compound	N_2	CO	CH_4	CO_2
molar %	2.58	7.60	81.63	8.20

Table 5.28. Composition of Reactor Gas upon Recycle

Pressure = 38 atm Temp. = 317°C

Compound	O_2	N_2	CO	CH_4	CO_2	H_2O	CH_3OH
molar %	-	1.72	7.45	59.41	12.22	13.93	5.26

RECIRCULATION VII

Table 5.29. Oxidation of CH_4 with O_2 - Single pass mode

Reactor pressure = 34.1 atm Temp. = 330 ± 1°C

Flow Rate = 100 mL/min NTP ST(reactor = 390s (reac. vol)$^{-1}$

% O_2 conc. = 9.19 ± 0.15% % N_2 conc. = 9.30 ± 0.02

	O_2	N_2	CO	CH_4	CO_2	H_2O	CH_3OH
molar %	-	7.99	2.66	71.38	1.37	13.65	3.00
±		0.01	0.13	0.27	0.15	0.75	0.20
% selectivity (±)			37.78±0.56		19.40±0.90		42.80±0.32
C/N_2			0.33	9.04	0.17		0.38
O_2/N_2			0.16		0.17	0.86	0.19

% Conversion = 9.04 ± 0.01 % C. bal = 101.9 ± 0.73

% Yield = 3.85 ± 0.19

Table 5.30. Composition of Recycle system gas prior to Recycle

	N_2	CO	CH_4	CO_2
molar %	7.24	15.62	60.88	16.24
±	0.11	0.54	1.25	0.82

Table 5.31. Determination of CH_4 conversion prior to Recycle - Single pass mode

Input CH_4/N_2 = 9.75 ± 0.03 (6)* (Reactants)

Output CH_4/N_2 = 9.04 ± 0.08 (5) (Products)

Conversion = ((9.75 - 9.04)/9.75) . 100

= 7.32 ± 0.10 %

*number of determinations

Table 5.32. Determination of Recycle - Main feed CH_4 conversion undergoing Recycle

Input (Recycle-Main feed) CH_4/N_2 = 9.53 ± 0.08 (3) (Reactant)

Output CH_4/N_2 = 8.91 ± 0.08 (3) (Product)

Conversion = 6.50 ± 0.16%

Table 5.33. Oxidation of CH_4 with O_2 - Recycle mode

Reactor pressure = 34 atm Temp. = 330 ± 1°C

	O_2	N_2	CO	CH_4	CO_2	H_2O	CH_3OH
molar %	-	6.84	7.41	57.83	14.64	11.40	1.976
±		0.23	0.303	0.524	0.99	1.94	0.175
% selectivity ±			*		*		46.85±3.73**
C/N_2				8.47±0.28			0.29±0.02
O_2/N_2							

% Conversion = 11.17 ± 3.46

% Yield = 5.22 ± 1.44

*artificial

**average CH_3OH/N_2 yield relative to consumed CH_4/N_2 value in Table 5.32

Recirculation VIII

Table 5.34. Composition of Recycle System Gas Prior to Recycle.

System pressure = 27.4 atm

	N_2	CO	CH_4	CO_2
molar %	5.73	15.58	58.36	20.35

Table 5.35. Determination of CH_4 Conversion Prior to Recycle - Single Pass Mode

Input CH_4/N_2 = 15.36 ± 0.10(5)

Output CH_4/N_2 = 14.36 ± 0.22(4)

Conversion = (0.73/15.36) . 100 = 4.76 ± 0.33%

Table 5.36. Oxidation of CH_4 with O_2 - Single Pass Mode

Reactor Pressure = 36.4 atm Temp. = 312.5 ± 0.5°C

Reactor Flow Rate = 37.5 mL/min NTP S.T. reactor = 1190s

% O_2 conc. = 3.42 ± 0.07% % N_2 conc. = 6.11 ± 0.90

	O_2	N_2	CO	CH_4	CO_2	H_2O	CH_3OH
molar %	-	4.21	0.54	80.88	0.56	11.11	2.61
% selectivity			14.65		15.00		70.35
C/N_2			0.129	19.17	0.132		0.620
O_2/N_2			0.064		0.132	1.143	0.310

% Conversion = 4.17 % C. bal. = 130.52

% Yield = 2.93

Table 5.37. Determination of Recycle - Main feed CH_4 Conversion During Recycle

Feed pressure = 36.4 atm

Input (Recycle - Mainfeed CH_4) = 12.47 ± 0.03 (3)

Output CH_4/N_2 = 11.80 ± 0.04 (3)

Conversion = (0.66/12.47) . 100 = 5.33 ± 0.08%

Table 5.38. Oxidation of CH_4 with O_2 - Recycle Mode

Reactor pressure = 36.3 atm Temp = 312.5 ± 0.5°C

	O_2	N_2	CO	CH_4	CO_2	H_2O	CH_3OH
molar %	-	3.66	5.51	55.70	20.61	12.95	1.53
±		0.60	0.10	0.40	0.60	0.30	-
% selectivity ±			*		*		63.4±0.9**
C/N_2				15.19±0.17			0.42±0.01
O_2/N_2							

**CH_3OH selectivity = (0.42/0.66) . 100 (see Table 5.37 above) based on CH_4 conversion relative to N_2.

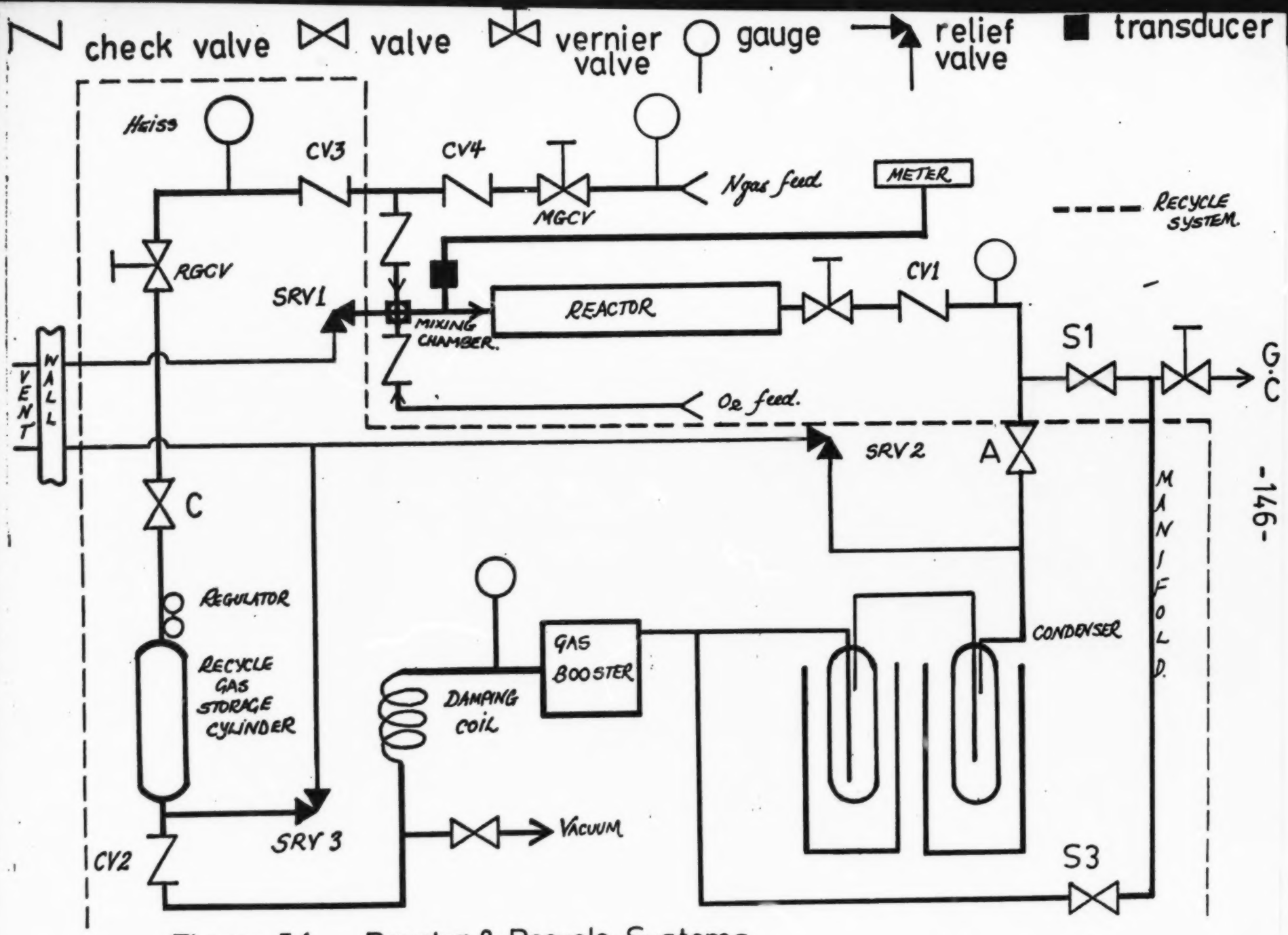


Figure 5.1 Reactor & Recycle Systems.

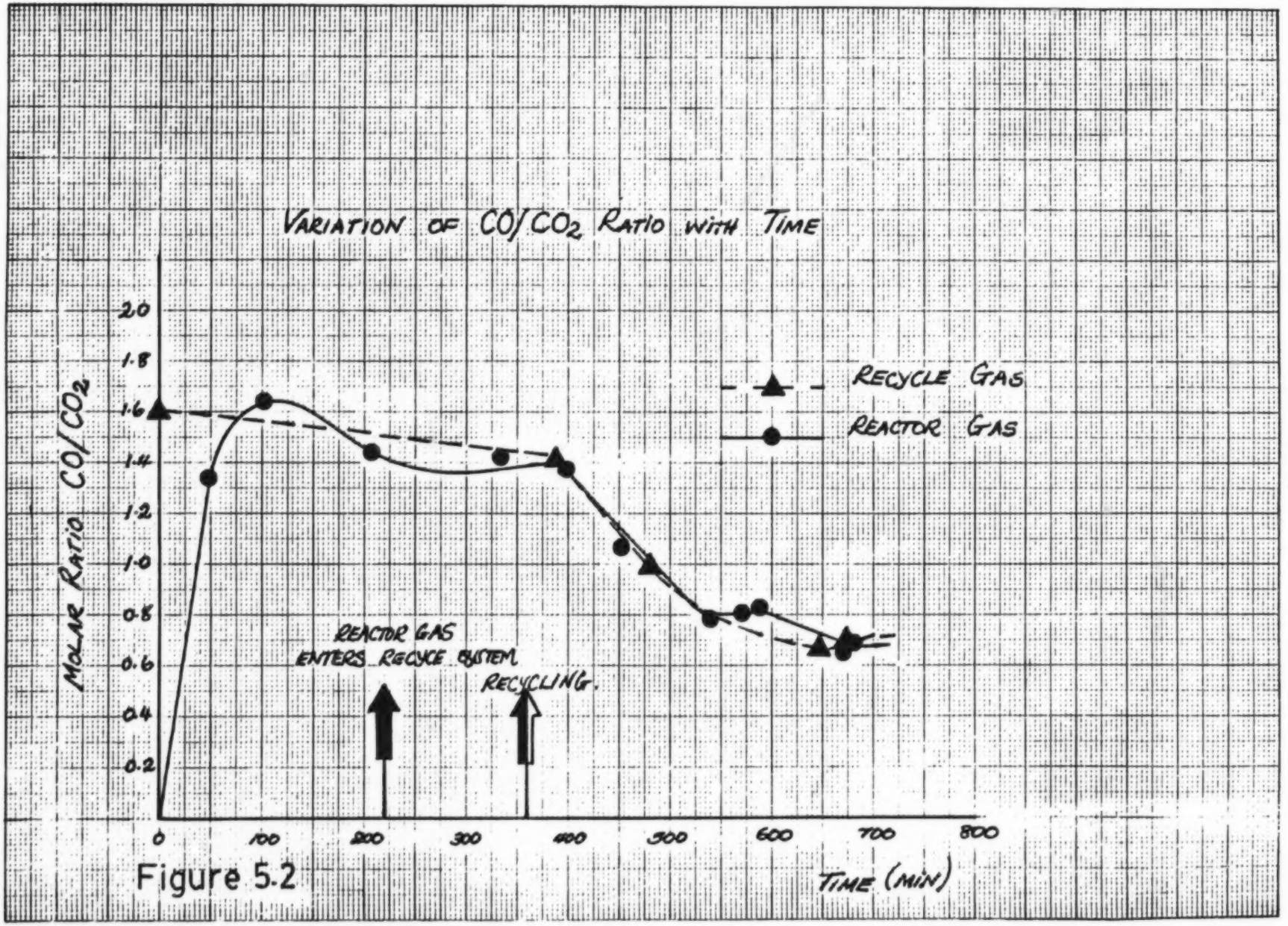

VARIATION OF CO/CO2 RATIO WITH TIME
MOLAR RATIO CO/CO2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
100
200
300
400
500
600
700
800
TIME (MIN)
RECYCLE GAS
REACTOR GAS
REACTOR GAS ENTERS RECYCLE SYSTEM
RECYCLING.

Figure 5.2

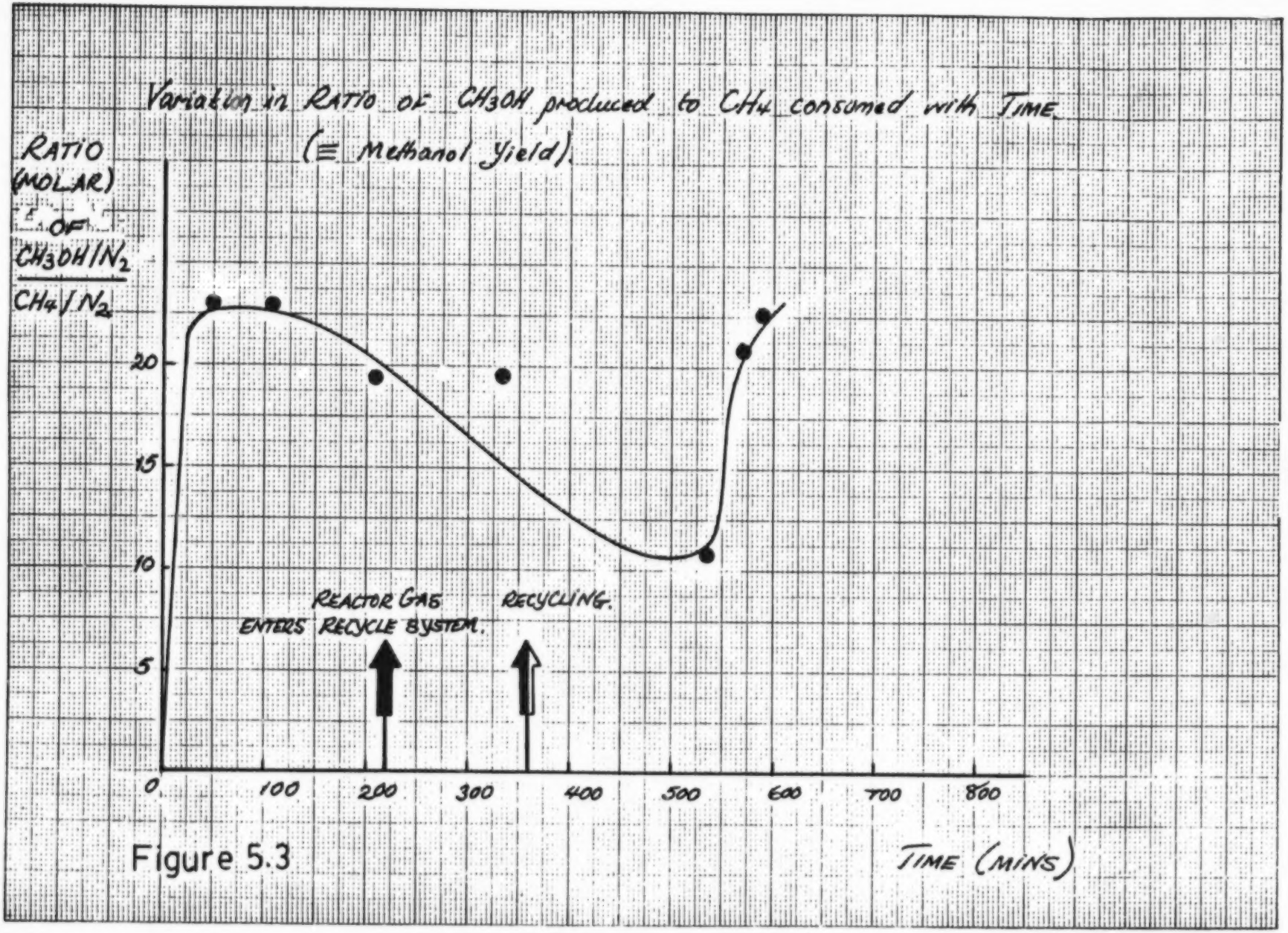


Figure 5.3

10 X 10 TO THE CM

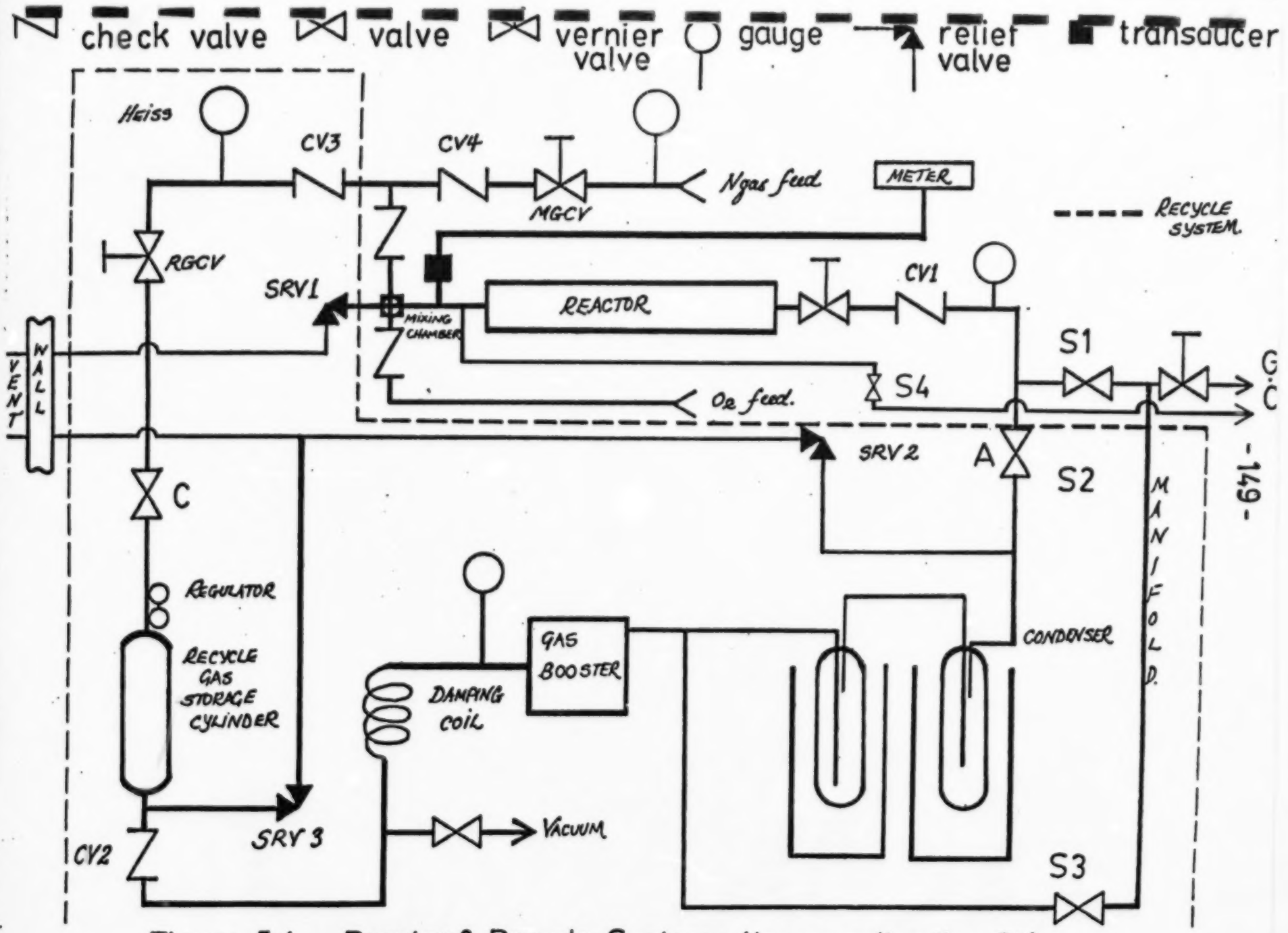


Figure 5.4. Reactor & Recycle Systems (inc. sampling line S4).